OXYGEN COMPATIBILITY TESTING OF COMPOSITE MATERIALS

Neil A. Graf
Richard J. Hudgins
Michael McBain

Lockheed Martin Space Systems Company – Michoud Operations
New Orleans, LA 70129

ABSTRACT

The development of polymer composite liquid oxygen (LO_2) tanks is a critical step in creating the next generation of launch vehicles. Future launch vehicles need to minimize the gross liftoff weight (GLOW), which is possible due to the 25%-40% reduction in weight that composite materials could provide over current aluminum technology. Although a composite LO_2 tank makes these weight savings feasible, composite materials have not historically been viewed as "LO_2 compatible." To be considered LO_2 compatible, materials must be selected that will resist any type of detrimental, combustible reaction when exposed to usage environments. This is traditionally evaluated using a standard set of tests. However, materials that do not pass the standard tests can be shown to be safe for a particular application. This paper documents the approach and results of a joint NASA/ Lockheed Martin program to select and verify LO_2 compatible composite materials for liquid oxygen fuel tanks. The test approach developed included tests such as mechanical impact, particle impact, puncture, electrostatic discharge, friction, and pyrotechnic shock. These tests showed that composite liquid oxygen tanks are indeed feasible for future launch vehicles.

1. INTRODUCTION

1.1 Need

The development of polymer composite liquid oxygen tanks is a critical step in creating the next generation of launch vehicles. Future reusable launch vehicles need to minimize the gross liftoff weight (GLOW) by reducing the dry mass fraction. The (dry) mass fraction is the weight of the launch vehicle without fuel divided by the weight of the vehicle with fuel. Figure 1 is graph showing the effect of mass fraction on GLOW. Indicated on the graph is a typical reusable launch vehicle (RLV) mass fraction target region as well as a mass fraction of the RLV without the weight reduction that composites could provide. Reducing GLOW would result in lower costs to orbit and increased payload capabilities, which in turn fulfills the goal of next-generation launch vehicles to make access to space more affordable. It is clear that composite tanks are critical to enable future launch vehicles to meet required mass fractions.

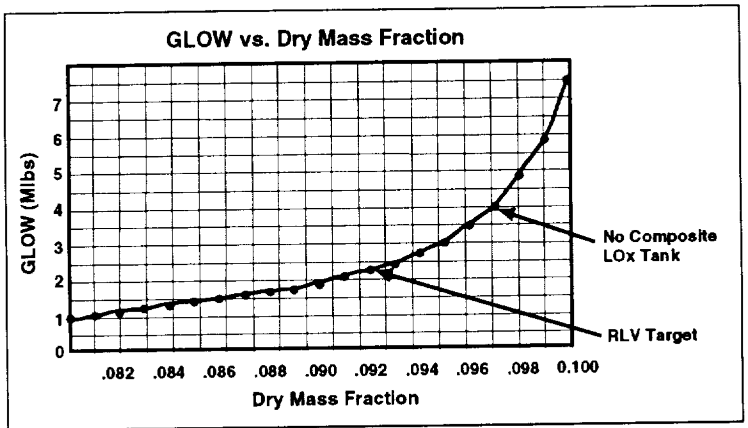


Figure 1: Effect of Mass Fraction on Gross Liftoff Weight

The required mass fraction is possible due to the reduction of weight that composite materials can provide. Traditional oxygen tanks are made from metals. The space shuttle external tank (ET) has historically been made from 2219 aluminum and more recently 2195-aluminum/lithium alloy. Figure 2 shows a comparison between these two aluminum alloys and a typical composite material for a liquid oxygen tank for a launch vehicle. The chart shows that a composite tank provides up to 40% and 28% weight savings when compared to 2219 and 2195 aluminum tanks, respectively.

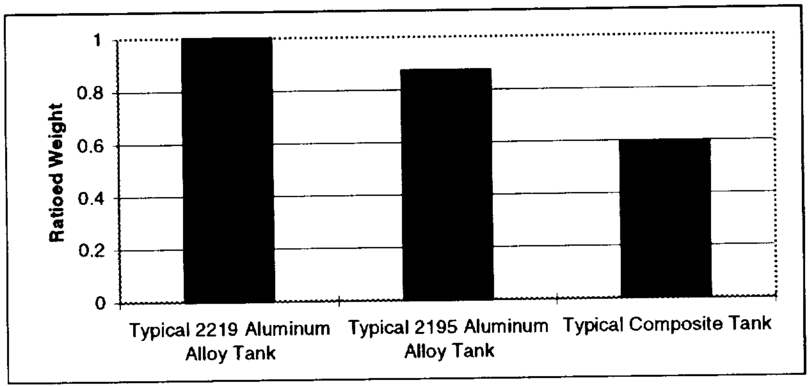


Figure 2: Material Weight Comparison

Composite feedlines can also provide weight savings, especially for advanced future launch vehicles (like VentureStar) that have forward oxygen tanks and aft engines. Preliminary weight analyses for VentureStar indicate that if only the straight sections of feedlines were switched to composite, a weight saving of over 680 kg (1,500 pounds) would result. Other feedline components (elbows, valve bodies, etc.) made of composites could result in an additional weight savings of 1360-2270 kg (3,000-5,000 pounds). Again, this would increase payload capability and decrease the cost of space access.

Although a composite LO_2 tank makes RLV mass fractions feasible and composite feedlines contribute additional weight savings, composite oxygen tanks and feedlines must be compatible with oxygen. The ASTM G4 committee defines oxygen compatibility as "the ability of a substance to coexist with *both* oxygen and a *potential* source(s) of ignition within the acceptable risk parameter of the user [at an expected pressure and temperature]". It is imperative that materials are selected that will resist any type of detrimental, combustible reaction when exposed to usage environments. Typically, non-metallic materials are not used in these applications because most are easily ignited in the presence of oxygen. Thus, the development of composite materials that are compatible with liquid oxygen is critical to the success of future launch vehicle programs.

1.2 General Statement on Oxygen Compatibility

The selection of a material for use in oxygen environments is primarily a function of understanding the circumstances that cause oxygen to react with the material. Composite materials in contact with oxygen will not react without a source of ignition energy. When an energy input rate is greater than the energy dissipation rate, ignition and combustion may occur. The material systems and the potential ignition/energy sources should be viewed in the context of the entire system design. In other words, the suitability for each material system for use depends on the particular application.

1.3 Historical Test Methodology

The traditional methodology (laid out in NASA-STD-6001, Section 2.2) is that materials used in LO_2 or gaseous oxygen (GO_2) environments must meet two criteria: Flammability and Impact Sensitivity. For the flammability requirement, a material must meet the criteria for either Test 1, "Upward Flame Propagation," or Test 17, "Upward Flammability of Materials in GO_2," as defined in the STD-6001 document. For impact sensitivity, the material must meet the requirement of Test 13A, "Mechanical Impact for Materials in Ambient Pressure LO_2," or 13B, "Mechanical Impact for Materials in Variable Pressure GO_2 and LO_2" as described in STD-6001. The impact test is also outlined in ASTM D2512. A similar impact test, such as the "Modified Mechanical Impact" test, may be substituted for Standard Test 13A or 13B with the approval of the end user and the responsible NASA center counterpart. The modified mechanical impact test is not currently included in NASA-STD-6001, but may be added in the future.

Should a composite material meet these requirements, it would be considered acceptable for use in liquid oxygen. No additional testing would be necessary. In other words, the composite material is considered inert and safe for use in oxygen environments even if ignition sources are present in the system. At the beginning of the X-33/RLV program in the summer of 1996, no composite material was able to meet these requirements. Therefore, an alternate testing methodology was established to test composite materials for LO_2 compatibility.

2.0 EXPERIMENTAL

2.1 Alternate Test Methodology

Early in the X-33/RLV test program, a team of oxygen compatibility and composite tank experts was assembled. This team included Lockheed Martin Space Systems Company, Michoud Operations, along with NASA's Johnson Space Center White Sands Test Facility (WSTF) and Marshall Space Flight Center (MSFC). The team established an approach for evaluating composite materials for liquid oxygen tankage.

NASA-STD-6001, section 2.2, and NASA NSS 1740.15, section 301(e), state that materials that do not meet the requirements of the traditional methodology must be verified to be acceptable in the use configuration and environment by analysis or testing and specifically approved by the responsible NASA center materials organization.

Figure 3 below summarizes the approach that was developed for composite materials. This approach is based on tests that have been selected to encompass most composite LO_2 tanks for most launch vehicles. In addition, a hazard analysis must be done to determine if additional testing is required for each specific application.

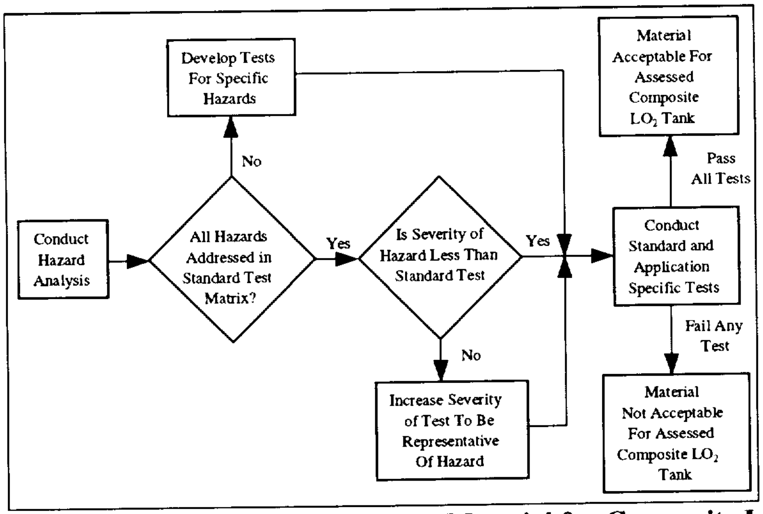
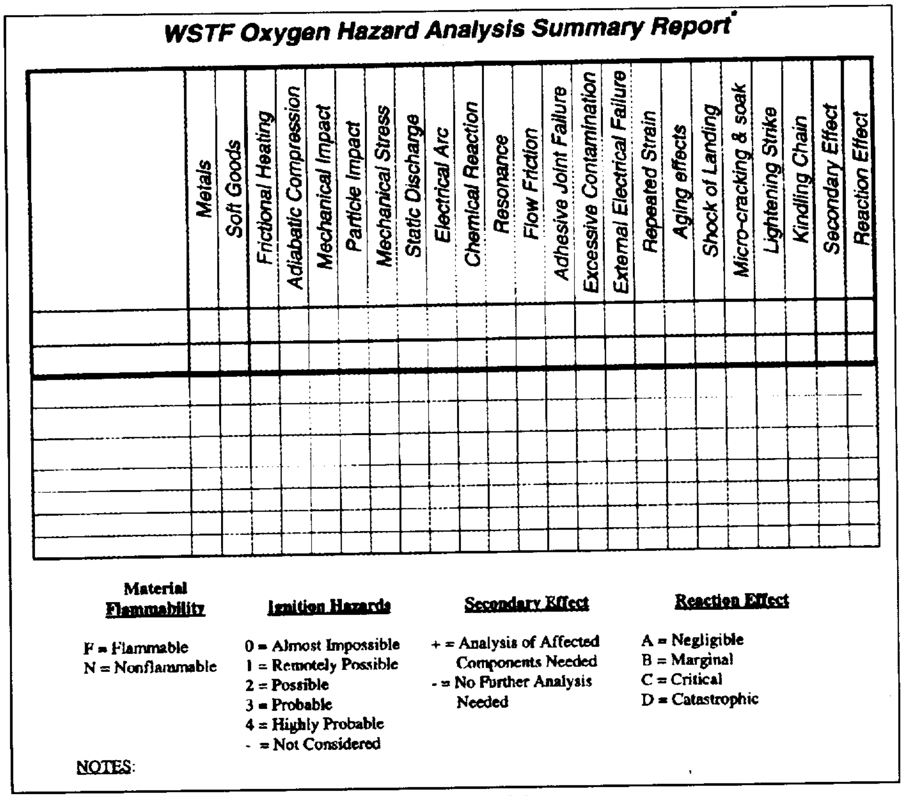


Figure 3: Approach for Approving Material for Composite LO_2 Tank

Lockheed Martin and NASA conducted a series of hazard analyses during the X-33/RLV program. NASA NSS 1740.15, Section 202, describes the procedure for conducting a hazard analysis. If desired, ASTM G63-92 can be used, which describes similar procedures for ignition mechanism evaluation and assessment. In general, a hazard analysis should be conducted per the following procedure. First, the oxygen application and investigation scope should be defined, and an appropriate hazard analysis team assembled. Then, operating conditions should be identified. Next, a determination of the materials' situational flammability (flammability at these conditions), presence of potential ignition should be complied on the component, and the worst case sources, and likelihood of secondary ignition hazards is made. After performing a reaction effects assessment reviewing any additional safety issues, any required testing is determined and additional safety recommendations made. A formal hazards analysis report, capturing the analysis results and recommendations, is then generated and distributed to all involved parties. A table, as seen in Figure 4, is often used in the report to summarize the hazard analysis.



WSTF Oxygen Hazard Analysis Summary Report*

	Metals	Soft Goods	Frictional Heating	Adiabatic Compression	Mechanical Impact	Particle Impact	Mechanical Stress	Static Discharge	Electrical Arc	Chemical Reaction	Resonance	Flow Friction	Adhesive Joint Failure	Excessive Contamination	External Electrical Failure	Repeated Strain	Aging effects	Shock of Landing	Micro-cracking & soak	Lightening Strike	Kindling Chain	Secondary Effect	Reaction Effect

Material Flammability	Ignition Hazards	Secondary Effect	Reaction Effect
F = Flammable N = Nonflammable	0 = Almost Impossible 1 = Remotely Possible 2 = Possible 3 = Probable 4 = Highly Probable - = Not Considered	+ = Analysis of Affected Components Needed - = No Further Analysis Needed	A = Negligible B = Marginal C = Critical D = Catastrophic

NOTES:

Figure 4: Hazard Analysis Summary Table

When assessing the most severe operating conditions and their effects on the system, the condition parameters must be defined. These parameters include, but are not necessarily limited to, pressure, temperature, oxygen concentration, flow velocity, and mission life/number of cycles. If the most severe condition cannot be determined, a range of operating conditions should be considered.

A wide array of ignition sources should also be considered and ranked in the analysis. A list of potential ignition mechanisms (by no means comprehensive) identified in NASA NSS 1740.15 is shown in Table 1 below.

Table 1: List of Potential Ignition Mechanisms from NASA NSS 1740.15

Adiabatic compression	Generation of electrical charge by equipment operations
Personnel smoking	Thermal ignition
Shock waves from tank rupture	Open flames
Heating of high-velocity jets	Fragments from bursting vessels
Explosive charges	Welding
Resonance ignition (repeated shock waves in flow system)	Friction and galling Mechanical impact
Tensile rupture	Mechanical vibration
Exhaust from thermal combustion engine	Particle impact
Electrical ignition	Electrical short circuits, sparks, and/or arcs
Metal fracture	Static electricity (two-phase flow)
Static electricity (solid particles)	Lightning

The hazard analyses performed for composite materials in VentureStar applications led to a two-phased approach. The first phase was to perform the standard NASA-STD-6001 Test 13A, Standard Mechanical Impact, as a screening test. The leading material candidates would then undergo a second phase of characterization tests. Table 2 provides a list of these tests outlined for composite materials. The acceptance criteria listed in Table 2 were set for the purpose of this study only, and are not necessarily the same as those listed in NASA-STD-6001.

Table 2: Standard Test Matrix for Approving Composite Materials for LO_2 Tanks

Ignition Hazard	Test	Acceptance Criteria
Mechanical Impact at Ambient Pressure	Standard Mechanical Impact Test (STD-6001 Test 13A) in LO_2	For Information Only
Mechanical Impact at Ambient Pressure	Modified Mechanical Impact Test in LO_2	0 Reactions/20 Samples or 1 Reaction /60 Samples at 47 J (35 ft-lbs)
Mechanical Impact at Maximum Use Pressure	Pressurized Mechanical Impact (STD-6001 Test 13B) in LO_2 (100 psi)	0 Reactions/20 Samples or 1 Reaction /60 Samples at 47 J (35 ft-lbs)
Mechanical Impact at Maximum Use Pressure	Pressurized Mechanical Impact (STD-6001 Test 13B) in GO_2 (40 psi)	0 Reactions/20 Samples or 1 Reaction /60 Samples at 47 J (35 ft-lbs)
Friction Energy	MSFC Friction Test for Composites in GO_2	0 Reactions/10 Sample Sets Tested to Mechanical Failure
Puncture (Inside Tank to Outside	MSFC Internal Puncture Test in LO_2	0 Reactions/20 Samples Tested
Puncture (Outside Tank to Inside)	MSFC External Puncture Test in LO_2	0 Reactions/20 Samples Tested
Static Electricity/ Other Electrical Charge	MSFC Electrostatic Discharge (ESD) in GO_2	0 Reactions/20 Samples Tested
Shock Waves/ Resonance	MSFC Pyrotechnic Shock in LO_2	0 Reactions/10 Samples Tested
Adhesive Bond Failure	WSTF Adhesive Pull Test in LO_2	0 Reactions/18 Lap Shears Mechanically Failed
Particle Impact	WSTF Particle Impact Test in GO_2	0 Reactions/20 Samples Tested
Open Flames (Flammability)	Upward Flammability of Materials in GO_2 (STD-6001 Test 17)	For Information Only
Material Self-ignition if Heated in GO_2	Autoignition Test (AIT)	For Information Only
Ignition of Nearby Materials if Burning	Heat of Combustion	For Information Only

2.2 Screening Testing

2.2.1 Test Preparation: Material system candidates were selected after extensive searches of available NASA data, including data from MAPTIS (Materials and Processes Technical Information Systems), and vendor data. Candidate selections were based on flammability resistance, relative chemical inertness, process maturity, and prior usage in the aerospace industry. Materials selected for the screening tests included neat resins, polymer composites, polymer films, and lined or coated composites.

All samples were disks, 1.6 cm (0.625 ± 0.010 inches) in diameter. The thicknesses of the neat resin samples were 0.3 cm (0.125 ± 0.020 inches). Thicknesses of the composites were as-manufactured, ranging from 0.2 to 0.4 cm (0.085 to 0.150 inches). Thicknesses of the films were as-manufactured. Thicknesses of the coated and lined composites were the thickness of the composite plus the thickness of the additional material.

Mechanical impact tests were performed using an ABMA-type drop tester as shown in Figures 6a and 6b. Tests were conducted in accordance with ASTM D2512, which specifies the procedure for Test 13A of NHB 8060.1C. The tests were performed in the following manner. A sample of the test material was placed in a specimen cup, precooled and covered with liquid oxygen, and placed in a cup holder located in the anvil region assembly of the impact tester. A precooled striker pin was then centered in the cup. The plummet was dropped from selected heights onto the pin, which transmitted the energy to the test specimen. Observation for any reaction was made and the liquid oxygen impact sensitivity of the test material was noted. Drop tests were continued using a fresh specimen cup and striker pin for each drop, until the threshold value was achieved. A series of drop test were conducted at an energy level of 98 J (72 ft.-lbs.) and at lower intervals where necessary for the no reaction threshold.

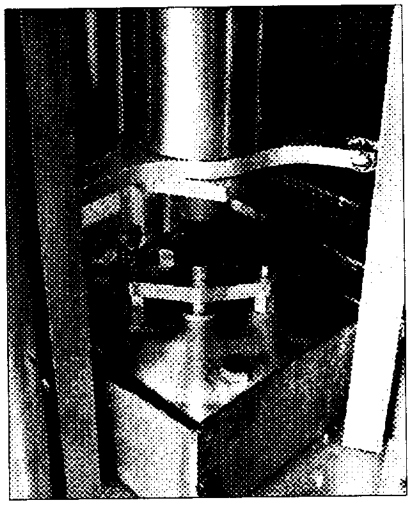


Figure 6a: Mechanical Impact Test Apparatus Photo

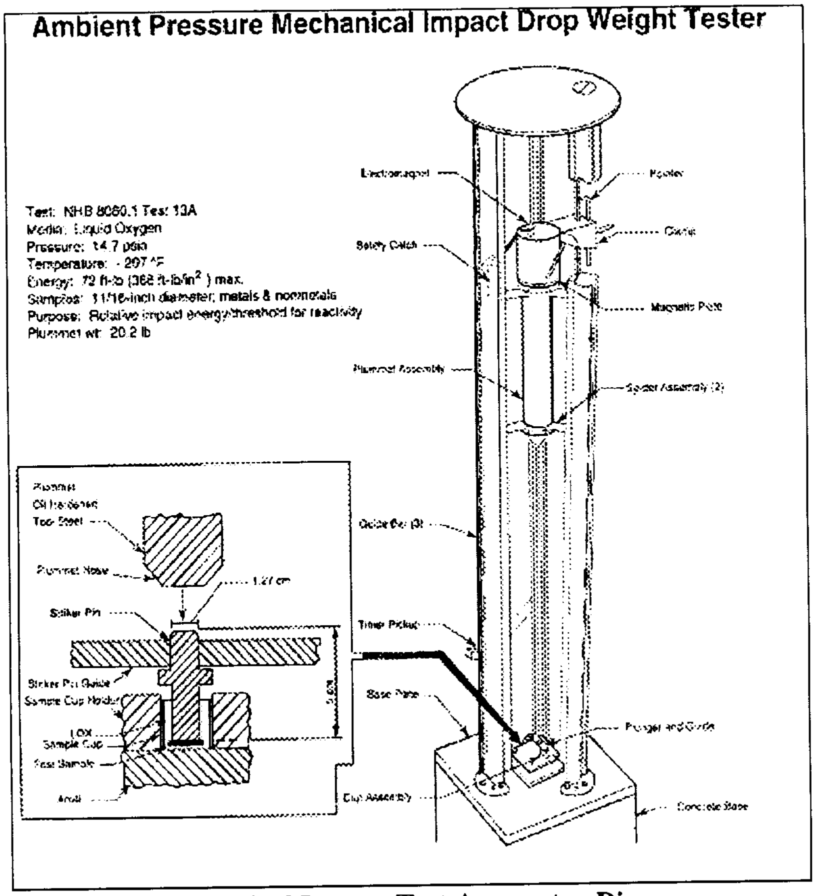


Figure 6b: Mechanical Impact Test Apparatus Diagram

A reaction is a chemical change or transformation in the sample caused by a mechanical impact. A reaction from mechanical impact can be determined by an audible report, an electronically or visually detected flash, or obvious charring of the sample, sample cup, or striker pin. Any of the following shall constitute reactions: (1) audible explosion, (2) flash (electronically or visually detected), (3) evidence of burning (obvious charring), and (4) major discoloration (due to ignition only rather than other phenomena).

2.2.2 Neat Resin Results: Testing of neat resin candidates was conducted at the two NASA centers. Twenty neat resin candidates were tested.

The thresholds for the neat resins are shown in Figure 7. The highest resin tested had a threshold of 0/20 reactions at 81 J (60 foot-pounds). The next best neat resin had a reaction threshold of 75 J (55 foot-pounds), followed by 1 resin each at 68, 61, 54, and 47 J (50, 45, 40, and 35 foot-pounds). Four resins passed at 40 J (30 foot-pounds), while another four passed at 34J (25 foot-pounds). Seven sets of resin candidates passed at 14 J (10 foot-pounds), while one candidate had no measurable threshold; the samples were reacting at the lowest test level.

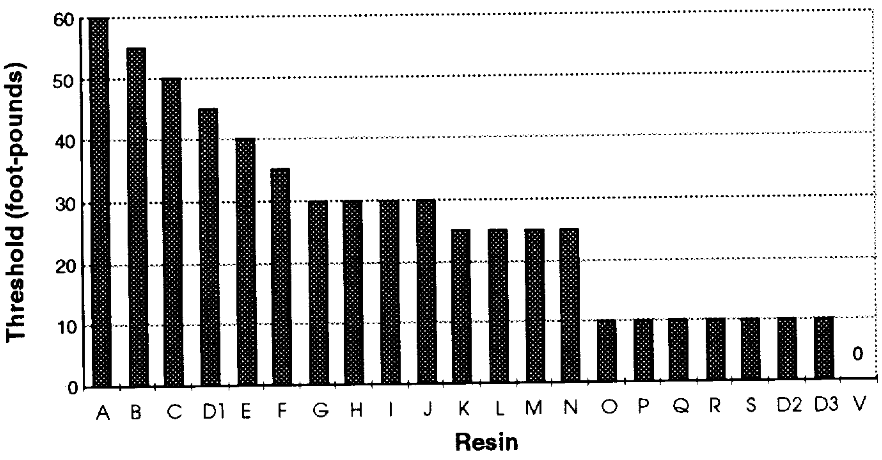


Figure 7: Neat Resin Thresholds

2.2.3 Composite Laminate Results: Many of the resins tested were also tested in composite laminate form. In this form, the resins were reinforced by aerospace-grade carbon fibers. Four candidates (AA, BB, CC, and DD) were tested in composite form only. Candidates X, Y, and Z are coated candidates. In general, the introduction of carbon fibers to the resins that were tested caused the reaction thresholds to be lower than that of the resins alone. Notable exceptions, however, are materials H and Q. As composite systems, H and Q with graphite fiber actually performed better than their corresponding neat resin samples tested.

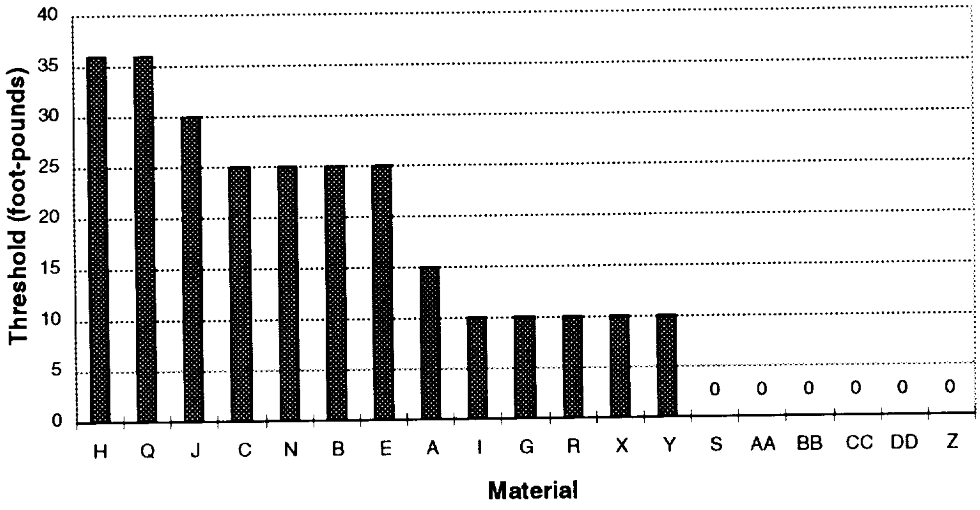


Figure 8: Composite Threshold

2.3 Characterization Testing

2.3.1 Test Preparation: Upon review of the available screening data, this list was downselected to five candidate systems. These systems were re-assigned the letters A-E, respectively. These materials were selected based on the Phase 1 data as well as engineering assessments of material properties and processing.

Phase 2 consisted of several types of testing. MSFC performed tests that were developed expressly for testing polymer composites. These tests include puncture, puncture of previously damaged specimens, friction, ESD (electrostatic discharge) and pyrotechnic shock. WSTF performed more standardized tests that included pressurized mechanical impact in LO_2 and GO_2, particle impact, flammability, autoignition temperature, and heat of combustion. More developmental tests performed at WSTF included adhesive pull and modified mechanical impact.

2.3.2 Characterization Test Results: The results of the characterization testing are summarized in Tables 3 and 4 below.

Table 3: NASA Marshall Space Flight Center Data

Test	A	B	C	D	E
External Puncture (undamaged)	0/20	0/20	0/20	0/20	0/20
Internal Puncture (of damaged LO_2 soaked)	0/20	0/20	0/20	0/20	0/20
Electrostatic Discharge	0/20	1/20	0/20	0/20	0/20
Friction	0/20	0/20	0/20	0/20	0/20
Pyrotechnic Shock	0/10	0/10	0/10	0/10	0/10

Table 4: NASA White Sands Test Facility Data

Test	A	B	C	D	E
Adhesive Pull	0/18	0/18	0/18	0/18	0/18
Particle Impact	0/20	2/20	0/20	0/20	0/20
Modified Mechanical Impact (40 ft-lbs)	1/16	0/20	0/20	0/20	0/20
Mechanical Impact in Pressurized LO_2 (100 psia)	0/20	0/20	0/20	0/20	0/20
Mechanical Impact in Pressurized GO_2 (40 psia)	0/20	0/20	0/20	0/20	0/20
Flammability at 14.7 psia (Burn Time in Seconds)	104-118	103-123	186-224	159-184	154-166
Autoignition Temperature	> 842°F	> 842°F	> 842°F	> 842°F	> 842°F
Net Heat of Combustion (MJ/kg)	28.49	28.29	28.94	27.13	29.66

3.0 CONCLUSIONS

3.1 Screening Test Conclusions

The screening tests yielded several interesting conclusions. First, thresholds have been generated for a variety of polymers and polymer composites. Although no structural resin or composite tested passed at 98J (72 foot-pounds), multiple materials passed at levels up to 75J (55 foot-pounds). This indicated a resistance to ignition and that a composite LO_2 tank is not outside the realm of possibility. Also, neat resin samples generally had a higher impact level than the composite samples made from those resins.

Next, the standard mechanical impact test was of limited value for composites, possibly due to edge effects. The lined and coated samples, probably due to limitations of the test, performed disappointingly in this test. The test results seemed to have high variations and were not necessarily repeatable for a given candidate. This, in turn, led to the development of the modified mechanical impact test in the characterization phase to help get away from these limitations.

3.2 Characterization Test Conclusions

The following conclusions were drawn from analysis of the Phase 2 data. Most importantly, composite materials showed the ability to withstand simulated hazards to a tank without igniting or burning, thereby demonstrating a high potential for an unlined composite LO_2 tank for RLV. Second, the candidate materials had equivalent performance in the specified environments in the majority of tests performed. In the following tests, no samples of any of the candidate materials reacted: pressurized impact in LO_2, pressurized impact in GO_2, adhesive pull, internal puncture of damaged specimens, external puncture, friction, and pyroshock. Similarly, no materials spontaneously combusted in the autoignition temperature test up to the fixture limit of 450°C (842°F). Results from four tests can be used to discriminate between a composite material's ability to resist reactions. These tests include flammability, modified mechanical impact, particle impact, and electrostatic discharge (ESD). In the particle impact and ESD tests, material B was the only material to react. None of the other materials reacted in these tests. Material A demonstrated lower thresholds in the modified mechanical impact test than any other candidate. All materials burned completely in a 100% GO_2 atmosphere when ignited. However, different materials burn at different rates. Composite material C took the longest to burn. All materials had higher impact thresholds in the modified mechanical impact test than the ambient mechanical impact tests from Phase 1. This seems to indicate that edge effects, which are eliminated in the modified test, do have an effect on the test results. All candidates passed the pressurized mechanical impact test with a threshold of 98 J (72 foot-pounds). This was considerably higher than the materials' threshold levels in ambient mechanical impact tests in Phase 1. From the discriminator tests, several composite materials are compatible for LO_2 tankage use.

4. REFERENCES

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