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14. ABSTRACT

Parmax®, a self reinforcing ultra-high performance polymer, was investigated as an ablative material in ramjet combustor applications. Phase I effort has demonstrated that Parmax® SRP materials offer a number of advantages over the existing ablative solution. These include 1) Superior erosion rate performance 2) Better insulative properties 3) Lower ablative material density 4) Superior mechanical properties and 5) Lower or comparable cost (in commercial stage). Phase I demonstrated the extraordinary promise of Parmax® SRP materials as ablative insulators. In order to successfully transport this fundamental, material science promise into the complex rocket motor system environment. The Phase II effort will focus on final material optimization, filling out the gaps in design data and perhaps most importantly, familiarizing engine designers with the promise of these unique materials.

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EXECUTIVE SUMMARY

During Phase I, Mississippi Polymer Technologies, Inc. (MPT) proposed to evaluate its Parmax® Self-Reinforced Polymers ("SRPs") as ablative materials for ramjet combustor applications. Parmax® SRPs, which offer strengths comparable to mild steels and specific strengths comparable to titanium alloys, are thermoplastic polyparaphenylenes with excellent ablative and mechanical properties. During Phase I we proposed to execute the following tasks:

TASK I:	Compound Parmax® SRPs into formulations suitable for ramjet combustor applications and fabricate Task II test specimens;
TASK II:	Characterize Parmax® SRP test specimens from Task I to identify specific formulations for advanced development; and
TASK III:	Enter into collaboration with one or more existing manufacturers of air-breathing rocket engines for subsequent development and testing work.

In the course of performing these tasks, we have demonstrated that Parmax® SRP-based ablative systems possess a series of advantages over the existing solution (Dow Corning 93-104) such as:

- Superior erosion rate (< 0.83 mils/sec versus 2.5 mils/sec for 93-104 per ASTM E285)
- Greatly increased insulative properties (18 s/mm insulation index vs. 1 s/mm for 93-104)
- Reduced ablative material density (79 lb/ft^3 vs. 91 lb/ft^3 for 93-104)
- Orders of magnitude greater strength before and after the burn
- Parmax® SRP (at commercial stage) will be lower than or comparable in cost to 93-104

Based on these results (detailed in this Report), even a simple drop-in replacement of a Parmax® SRP ablative system would yield a number of benefits including better ablative performance, lower overall system weight and cheaper system assembly.

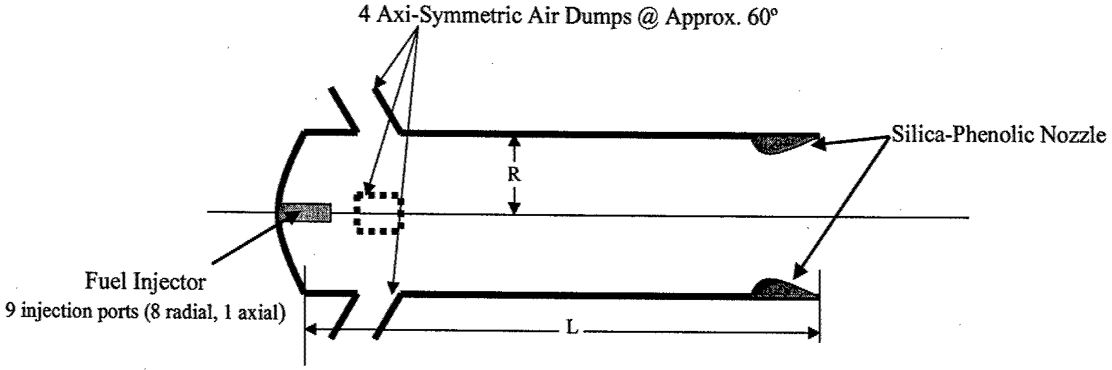
Revolutionary advances, however, can be expected once designers take full advantage of the superior properties of the new system. Greatly increased insulative properties of Parmax® SRPs, for example, may lead to increased combustion chamber temperatures, leading to increased range and/or payload. Alternatively, one could envision reduction in the overall system weight since the thickness of the insulation can be reduced due to the superior erosion rate and heat barrier properties of the improved system.

Finally, by combining the superior ablative and mechanical properties of Parmax® SRPs, it is potentially foreseeable that the entire ramjet combustor could be fabricated out of Parmax® SRPs, eliminating the insulated steel case. This elegant solution would provide tremendous system performance benefits, including increased range/payload, reduced logistical cost due to lighter weight, and potentially reduced lifecycle cost due to elimination of corrosion concerns.

Summarizing, during Phase I we demonstrated the extraordinary promise of Parmax® SRP materials as ablative insulators. In order to successfully transport this fundamental, material science promise into the complex rocket motor system environment. The Phase II effort will focus on final material optimization, filling out the gaps in design data and perhaps most importantly, familiarizing engine designers with the promise of these unique materials.

BACKGROUND

The simplest of all air-breathing engines is the ramjet. As shown schematically in Figure 1, it consists of a diffuser, a combustion chamber, and an exhaust nozzle. Air enters the diffuser where it is compressed before being mixed with the fuel and burned in the combustion chamber.[1] Combustion raises the temperature of the mixture to 3500°F before the products of combustion expand to high velocity in the nozzle.



$$L/(2R) = 3 \rightarrow 7$$

This Dimension will vary depending on Engine Sizing

Figure 1. Schematic diagram of ramjet

One of the main limitations on ramjet efficiency is the maximum operating temperature, which is directly correlated to the properties of the materials of fabrication. Ablative cooling is one method of protecting the ramjet combustion chamber (typically steel such as 17-4 Stainless or D6-AC) while operating at high temperatures. The current ablative insulation of choice, Dow-Corning 93-104, is a pourable, two-part silica- and carbon fiber-filled silicone rubber that is placed directly on the chamber. Unfortunately, this material is heavy, is comprised of two carcinogenic mixtures, and is not amenable to modern, high throughput forming techniques (extrusion, molding). As we will show, Parmax® SRPs offer the potential to solve all of these issues, in addition to providing superior ablative and insulative performance.

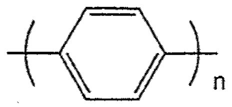


Figure 2. Polyparaphenylene

The extraordinary properties of Parmax® SRPs are a result of their revolutionary structure, as shown in Figure 2. Parmax® SRPs are based on materials that are considered the prototypical example of a strong, inert, and thermally stable organic polymer - polyparaphenylene. Polyparaphenylenes are elegantly simple and potentially inexpensive, deriving structurally from benzene. The repeat unit has exceptional chemical and thermal stability. These properties were

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[1] P.G. Hill and C.R. Peterson, *Mechanics and Thermodynamics of Propulsion.* Addison-Wesley, 1970, pp. 149-157.

the driving force for the study of rigid-rod systems, an active area of research for more than three decades.[2]

Unfortunately, until the advent of Parmax® SRPs, all of the existing routes to polyparaphenylenes have produced materials that were either highly impure, too expensive, too low in molecular weight, or lacked the processibility needed for structural applications.

Parmax® SRPs are prepared by a proprietary process which assures the isomeric integrity of the rigid-rod structure, and homopolymers or copolymers can be readily prepared. A variety of substituent groups "R" can be utilized, which, as suggested in Figure 3, are generally believed to adopt a nearly random orientation along the polymer backbone.

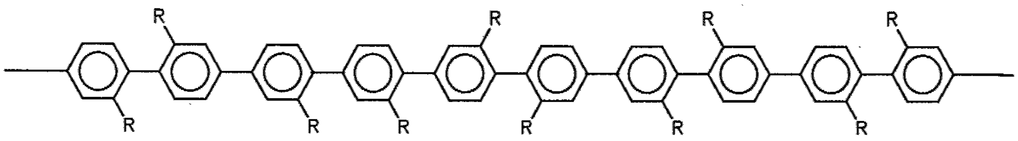

Figure 3. Generalized Structure of Rigid-Rod Parmax® SRPs

Parmax® SRPs are a class of polymers, like polyimides, polyesters, and polyamides, within which a wide range of structural variation is possible and are thus expected to be quite versatile. Typical members include Parmax®-1000 (benzoyl side groups with *para* linkages) and Parmax®-1200 (benzoyl side groups with a precise number of *meta*-substituted linkages). Figure 4 shows the structures of these derivatives.

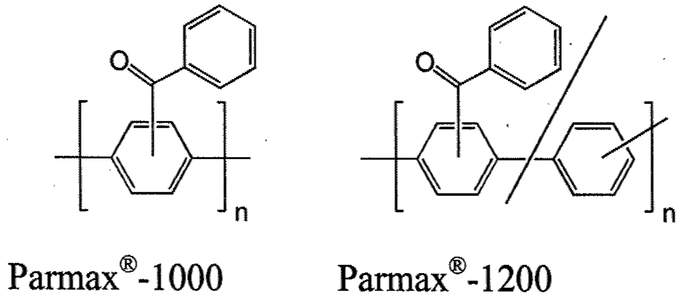

Figure 4. The Structures of Parmax®-1000 and Parmax®-1200

The benzoyl side groups and meta-substituted links (Parmax® 1200) are designed to impart solubility and melt processibility. The solubilizing side-groups also allow for the preparation of high molecular weight Parmax® SRP polymers, contrasting earlier attempts to prepare unsubstituted Polyparaphenylenes that resulted in low molecular weight materials due to limited growth of the insoluble oligomers.

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[2] a) Marvel, C. S. and Hartzell, G. E., *J. Am. Chem. Soc.,* 81, 448, (1959); Marvel, C. S. , Ray, S. , and Cassidy, P. E. , *J. Polymer Sci.,* A-3 (1965): b) Kovacic, P. and Jones, M. B. , *Chem.Rev.,* 87, 357 (1987); and references therein: c) Noren, G. K. and Stille, J. K., *J. Polymer Sci.* Part D, 5, 385 (1971); and references therein: d) van Kerckhoven, H. F., Gilliams, Y. K. and Stille, J. K., *Macromolecules,* 5, 541 (1972): e) Ballard, D. G. H., Courtis, A., Shirley, I. M., and Taylore, S. C., *J. Chem. Soc., Chem. Comm.,* 954 (1983): f) Noll, A., Siegfried, N. and Heitz, W., *Makromol. Chem.; Rapid Commun.,* 11, 485 (1990): and g) Miller, T. M., Neeman, T. X., Zayas, R. and Blair, H. E., *J. Am. Chem. Soc.,* 114, 1018 (1992).

Parmax® SRP Mechanical Properties

The mechanical and physical properties of Parmax® SRP polymers are unique when compared with other structural materials. Although many commercially available thermoplastics can be easily processed, they uniformly lack sufficient strength, stiffness and fire resistance properties to fulfill the requirements for many demanding defense applications. As demonstrated in Figure 5, isotropic Parmax® SRP resins possess unparalleled mechanical strength and modulus when compared to other high performance resins such as polycarbonate (e.g. Lexan®), acrylics, polyphenylene sulfide, polyurethanes, polyetherimide (e.g. Ultem®), and polyetheretherketone (PEEK).

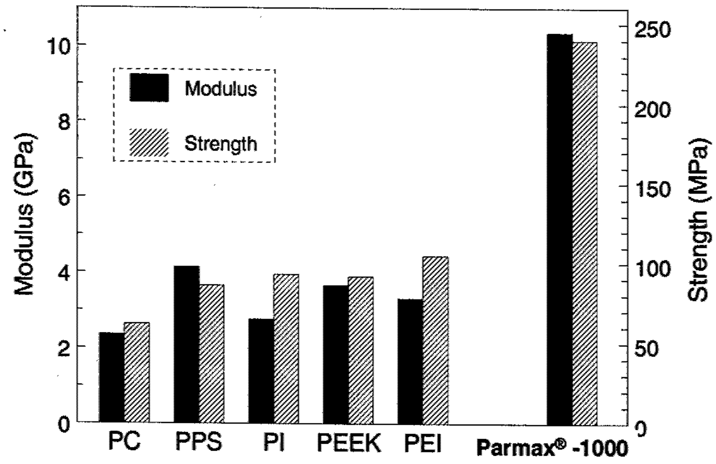
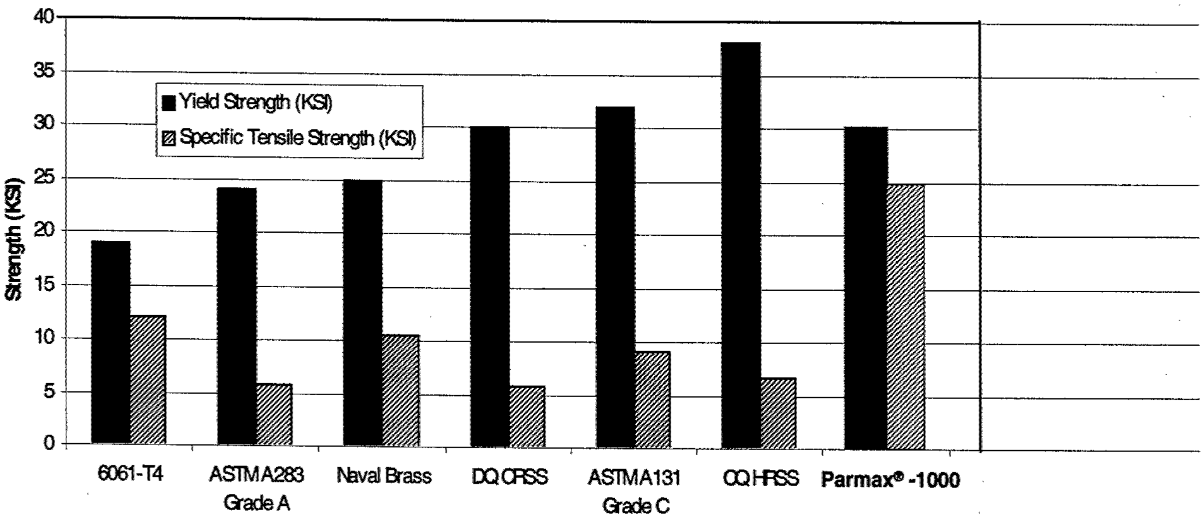


Figure 5. Mechanical Properties of Engineering Plastics and Parmax® SRP Resins

Properties of Parmax® SRP polymers are even more remarkable when compared to metals. Most polymers are severely hampered in structural and tribological applications owing to their inferior mechanical properties. Parmax® SRPs decisively overcome this handicap as illustrated in Figure 6 below



Drawing Quality Cold Rolled Sheet Steel and other metal values from ASM Metals Reference Book 2nd Edition

Figure 6. Comparative Strengths of Various Metals vs. Parmax® SRP Resin

Parmax® SRP polymers have strengths comparable to sheet steel on an **absolute** basis. This is truly remarkable when considering that Parmax® SRPs are transparent materials that are 7 times lighter than sheet steel materials. As a result, specific strengths of Parmax® SRP far exceed any of the common metals and are comparable to the best aerospace grades of titanium alloys.

Parmax® SRP resins are intrinsically safe to use because of their unique chemical nature. Unlike other high performance materials such as nitriles, imides, sulfones, or sulfides, Parmax® SRPs do not contain any nitrogen or sulfur. This is critically important, as nitrogen-containing compounds, including the highly stable polyphtalonitriles, have the potential to produce HCN gas and sulfur-containing compounds can produce H_2S, both of which are corrosive and toxic gases. The ultimate degradation products of Parmax® SRPs are simply water and CO_2.

Elementally simple chemical structure of Parmax® SRPs and their thermoplastic nature (eliminating the curing process) combine to offer a material which has no potential for off-gassing. This is important as usage of 93-104 has identified off-gassing as one of the chief contributors to weakening of the case/insulator bond-line interface.

Parmax® SRPs have Impressive Ablative Properties

Under service conditions, the ablation process includes the progressive endothermic decomposition of the fiber- or clay-reinforced organic materials together with mass flow of pyrolysis gases away from the heated surface, blocking heat flux to the outer surface. Accordingly, among the most important criteria for a useful ablative resin are high temperature stability, high char characteristics and no or few reactive degradation products as well as mechanical and environmental stability.

Parmax® SRPs and Parmax® SRP-based composite materials were expected to prove superior in all of these areas. Being aromatic, Parmax® SRPs possess a very high degree of thermal stability and show excellent charring characteristics with, for example, over 63% of weight remaining when Parmax®-1200 is heated to 1000°C under nitrogen atmosphere, Figure 7.

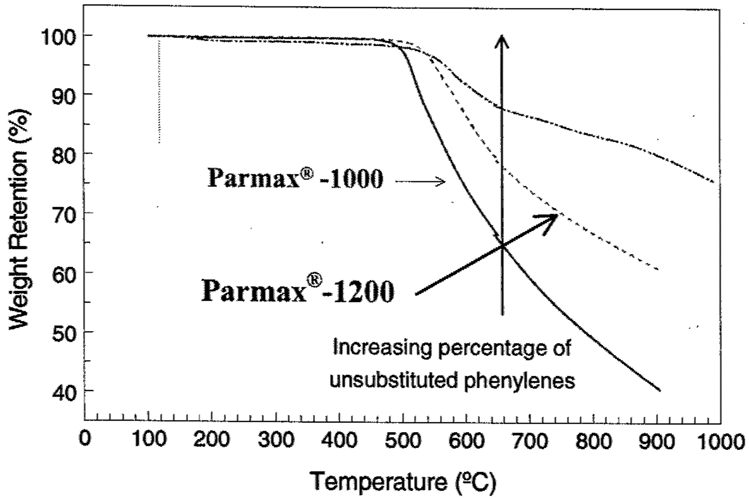


Figure 7. Parmax® SRP Thermal Stability (TGA)

Table 1 shows the results of a comparative ablative study performed by the Philips Laboratory at the Edwards Air Force Base. A lower number indicates superior ablative performance. At the high heat flux of 0.4 lb/in^{2}sec, Parmax® outperformed all the materials including clay filled Nylon-6. In addition, the ablation rate (in mils/sec) increases dramatically with increasing mass flux for both current standard ablative materials and the clay hybrids. In contrast, Parmax® SRPs appeared to be insensitive to mass flux. This property will have significant technological implications in the design, manufacture and utility of the proposed ablative materials.

Table 1. Phillips Laboratory Char Motor Ablation Rate Data

Type of Hybrid	High mass flux=0.4 lb/in^{2}sec **mils/s**
Standards and Controls	
EPDM/C/30% Silica	11
TKC's Pebax-TP Insulation	nvmr*
with 40% CHOP/pi fiber	15
Ultem	nvmr
Siltem	nvmr
Clay Hybrids	
Nylon-6	nvmr
Nylon-6/2% E-clay	nvmr
Nylon-6/2% E-clay/PI	9
Nylon-6/5% E-clay	10
Nylon-6/5% E-clay/PI	10
Vectra A950	nvmr
Parmax®-1000	**10**
Parmax®-1200	**8**

*nvmr = no virgin material remained

The results in Table 1 also confirmed that the ablative properties of any polymer are improved by compounding with either fibers or montmorillonite clay. Therefore, it was logical to assume that compounding Parmax® SRP resins with these materials would augment the already impressive ablative properties.

PHASE I TECHNICAL NARRATIVE

During Phase I, the primary technical objective was the initial determination of the suitability of Parmax® SRP-based materials for use as a ramjet combustor insulator. As outlined in the executive summary, this was divided into two Tasks:

TASK I: Compound Parmax® SRPs into formulations suitable for ramjet combustor applications and fabricate Task II test specimens;

TASK II: Characterize Parmax® SRP test specimens from Task I to identify specific formulations for advanced development

These two tasks presented the technical research portion of the effort, and they will be discussed in detail in this section. It is important to note that the overall effort was iterative in nature, with results from Task II guiding the subsequent iterations of Parmax® SRP formulations (Task I). As such, following the introduction, this Report will discuss the two tasks jointly.

Task I - Parmax® SRP Ablative Formulations

Parmax® SRP resins are truly revolutionary materials. However, there are limits to the properties achievable with organic polymer chemistry and architecture. Fortunately, these limits can be addressed to a great extent by compounding the neat resin with fillers and modifiers. This capability vastly extends the usability of the starting material and it was crucial for the success of this program.

Two additive materials widely known to improve the ablative properties of polymers are carbon fibers[4] and clay nanocomposites[5]. Prior tests with Parmax® SRP/carbon fiber compounded materials have proven that these materials possess excellent fire resistance properties eventually producing a rigid char. Additionally, work with Parmax®/clay mixtures has demonstrated the inclusion of Parmax®-1000 chains into the galleries of organo-modified clays thereby producing intercalated nanocomposites. These results guided the initial selection of additives during the execution of the Phase I effort.

The initial group of candidate additive materials for incorporation into Parmax® SRP ablative systems is given in Table 2.

Table 2. Materials compounded with Parmax® 1200 resin

Additive (Company)	Type
PA6, PA2 Fiber (Grafil)	Short Carbon Fiber
Closite 20A (Southern Clay Products)	Montmorillonite Clay
933 0.25" Glass Fiber (Hollex)	Glass Fiber
Kevlar® Fiber (DuPont)	Polyaramid Fiber
1 MM P-BOX Fiber (Toshoba)	Polybenzoxazole Fiber

The first step in fabricating compounded material was to identify the optimal method, that would properly disperse the additive throughout the polymeric matrix. Two initial compounding methods were investigated: melt mixing and polymer solution blending, both of which are described in detail in Appendix A.

Initial results comparing the two methods strongly suggested that the solution mixing method did a better job of compounding the materials than melt mixing. Solution mixed samples displayed consistently greater mechanical properties along with lower rates of erosion in initial flame impingement tests. This result is attributed to: 1) the ease of mixing additives into a low viscosity polymer solution versus a highly viscous polymer melt and 2) shortening of the effective fiber length during the melt compounding process owing to the high shear

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[4] Patton, R.L. et al.,*Composites Part A*, 33, 243 (2002).
[5] Vaia, R.A. et al., *Applied Clay Science*, 15, 67 (1999).

environments. The primary concern with using a solution-based method is the complete elimination of the flammable solvent. This issue was overcome with proper coagulation, rinsing and drying techniques.

Task 2 - Sample Characterization

The primary screening test carried out at MPT was ASTM E285 (direct oxy-acetylene torch testing) as shown in Figure 8. In this test, hot combustion gases (~ 2500°C / ~4500 °F) are directed along the normal to the specimen until burn-through is achieved. The erosion rate of the material is determined by dividing the original thickness by the time to burn-through.

ASTM E 285 has, over a number of years, been useful in determining the relative merit of materials, particularly in weeding out obviously poor materials. It has also been considered for use as a production quality-control test for rocket insulation materials. To normalize all of the results, the variation in thickness of all samples was kept to less than 1mm. Oxygen and acetylene pressures were kept constant at 20 psig and 5 psig, respectively. Burn through of each sample was determined through direct visual observation.

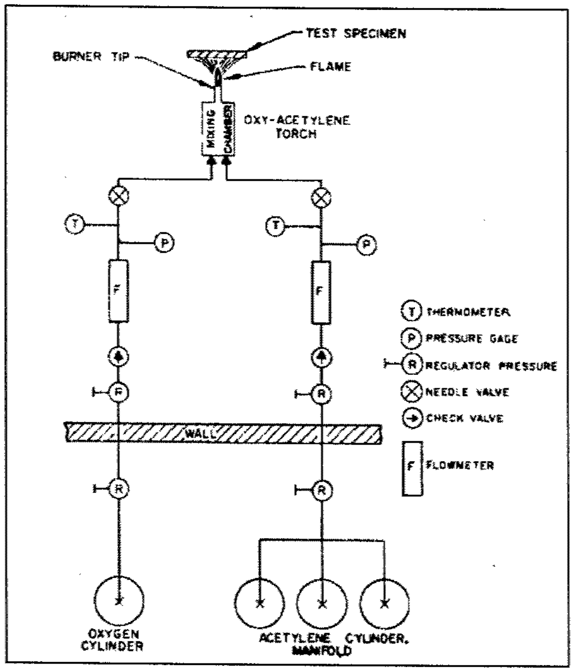


Figure 8. ASTM E285 torch test for screening candidate formulations/materials

Ramjet combustor materials are subjected to very high shear rates so it is imperative to test the physical properties (e.g. strength and density) of each sample. Mechanical properties of all candidate ramjet combustor materials are given in Table 3. The Parmax® 1200 samples all display approximately 100 times greater tensile strength as compared to the Dow Corning material, a significant factor in their superior ablative performance and char integrity.

Table 3. Properties of initial Parmax® SRP ablative formulations

Sample Description	Strength (KSI)	Density (pcf)	Erosion Rate (mil/sec)	Burn Through Time (s)
Dow Corning 93-104	0.043075	**91**	**2.5**	**97**
Parmax 1200	46.9	74	5.0	50
Parmax 1200 w/ 10% Clay	39.5	76	4.2	60
Parmax 1200 w/ 30% Carbon Fiber	42.8	**84**	**<0.83**	**NBT**
Parmax 1200 w/ 30% P-BOX Fiber	29.1	81	3.7	68
Parmax 1200 w/ 30% Kevlar Fiber	21.9	80	3.2	77
Parmax 1200 w/ 30% Glass Fiber	30.1	88	3.0	83
Post Burn:				
Charred Parmax 1200 w/ 30% Carbon Fiber	2.3	--		--

Table Key: NBT – No Burn Through

Remarkably, Parmax® SRP samples compounded with 30% carbon fiber were the only materials which displayed **no burn through** throughout the 120 second duration of the test. (Longer torch tests of ~ 5 minutes were done for the compounded Parmax® SRPs. In every case, no burn through was noted.) These ablative properties stand in stark contrast to the Dow Corning material, which burned through after approximately 100s of direct flame impingement

Another interesting result of this experiment was the impressive mechanical properties of the post-burn compounded Parmax® SRP sample. As shown in Table 3, the resulting char still had a degree of integrity while the post-burn Dow Corning sample was easily broken with a minimum of manually applied pressure. The preliminary torch test data gathered at MPT demonstrated that Parmax®-1200 compounded with 30% carbon fiber (CF) was an attractive potential replacement for Dow Corning 93-104 and was chosen for further testing.

Another aspect of Parmax® SRP formulations was the rapid extinguishing of flames after torch removal. By comparison, the Dow Corning material continued burning for well over 30s after testing was completed and the flame was removed. For the Parmax® samples, the flame was immediately extinguished after flame removal.

Thermophysical Testing

These initial Parmax® SRP/CF formulations were subjected to further thermal testing along with 93-104 samples. This was performed at the Laser Hardened Materials Evaluation Laboratory

(LHMEL) located at Wright-Patterson Air Force Base. This testing was arranged with cooperation from the Southern Research Institute. CO_2 lasers ranging in power from 15 kW to 135 kW produced thermal conditions comparable to those found within a ramjet combustor. High shear conditions were simulated by flowing air past the samples at Mach 0.5. This testing method allowed consistent and accurate measurements of thermal properties in a manner that was easily modeled due to the relatively simple and well-understood boundary conditions. Sample surface temperatures were measured using a pyrometer, and mid-plane and backface temperatures were measured using embedded K-type thermocouples.

The thermal responses of the compounded Parmax® sample and the Dow Corning 93-104 material were measured at 100 and 300 W/cm^2. The responses for 300 W/cm^2 are given in Figures 9 and 10. The results of the exposure to 100 W/cm^2 are very similar and discussion applies equally to them as well. The thermographs for 100 W/cm^2 can be found in Appendix B.

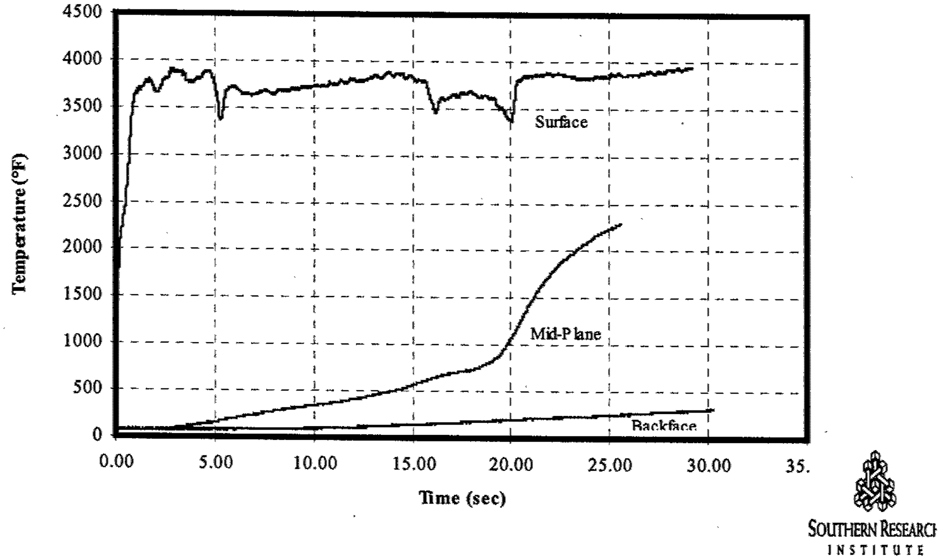


Figure 9. Response of compounded Parmax® at 300 W/cm² exposed for 30s. Flow: Mach 0.5.

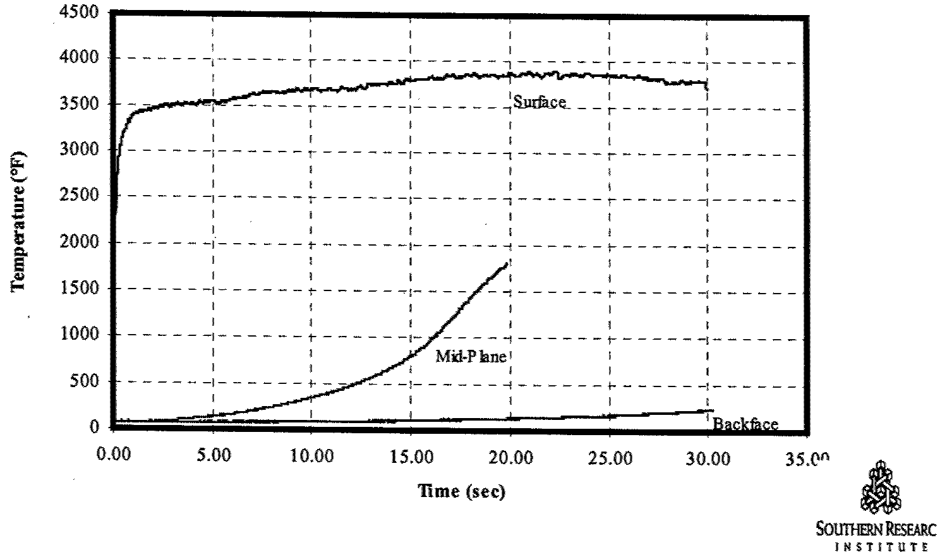


Figure 10. Response of Dow Corning 93-104 at 300 W/cm² exposed for 30s. Flow: Mach 0.5.

The most striking difference between the two materials is the much lower mid-plane temperature and rapid surface cooling and heating seen in the compounded Parmax® SRP material. Upon further investigation, it was noted that the Parmax® SRP samples swelled approximately 50% while the Dow-Corning material swelled 10%. The swelling is the result of entrapped decomposition gases within the polymer/carbon fiber/char matrix which can result in rapid cooling of the surrounding areas including the surface. As a result of the swelling, much lower mid-plane temperatures were recorded for the compounded Parmax® SRP samples along with approximately equivalent backface temperatures.

At the conclusion of this portion of our effort, the assessment of the initial Parmax® SRP/carbon fiber composites was as follows:

- Parmax® SRP formulation had superior erosion performance as per E285
- Parmax® SRP formulation had lower density (84 lbs/cm^3 vs. 91 lbs/cm^3)
- Parmax® SRP formulation had comparable insulative performance as measured by backside temperature performance
- Parmax® SRP formulation displayed more swelling than 93-104
- Parmax® SRP (at commercial stage) will be lower than or comparable in cost to 93-104

The second portion of the effort focused on elimination of the swelling issue encountered with the initial Parmax® SRP/CF formulation as well as on the improvement of the insulative properties. Both of these issues were addressed during the next iteration by changes in formulation as well as the fabrication method.

Elimination of the swelling was attacked first. The original, solvent-based, fabrication method was investigated and made more efficient. Longer carbon fibers were directly incorporated with the resin in the powder form. The fiber-impregnated resin was compression molded, thereby eliminating all the steps outlined in the solvent based scheme. The time needed for polymer dissolution, coagulation and drying were all eliminated resulting in an efficient fabrication scheme that is potentially ideal for mass production.

The longer fiber compression molded plaques displayed the same mechanical properties as the plaques fabricated by coagulation with solvents. Additionally these samples were as equally impervious to burn through as the solution based samples when tested per E285.

Most importantly, however, the swelling issue associated with the earlier generation of formulations was reduced to the level comparable to the Dow-Corning 93-104 material.

The second major issue we confronted was improvement in insulative properties of the Parmax® SRP ablative system. It was evident from the laser thermal testing that the compounded Parmax® SRP material possessed insulative properties that were very similar to the 93-104 material. The back-face temperature measurements of the Parmax® SRP material were nominally higher than the Dow-Corning 93-104 material, which can be explained by the difference in thermal conductivity values between the two substances. As shown in Figure 11, the thermal conductivity of the compounded Parmax® SRP material is approximately 50% higher than the Dow-Corning material and would explain the slightly higher backface temperature profile seen in the thermal tests.

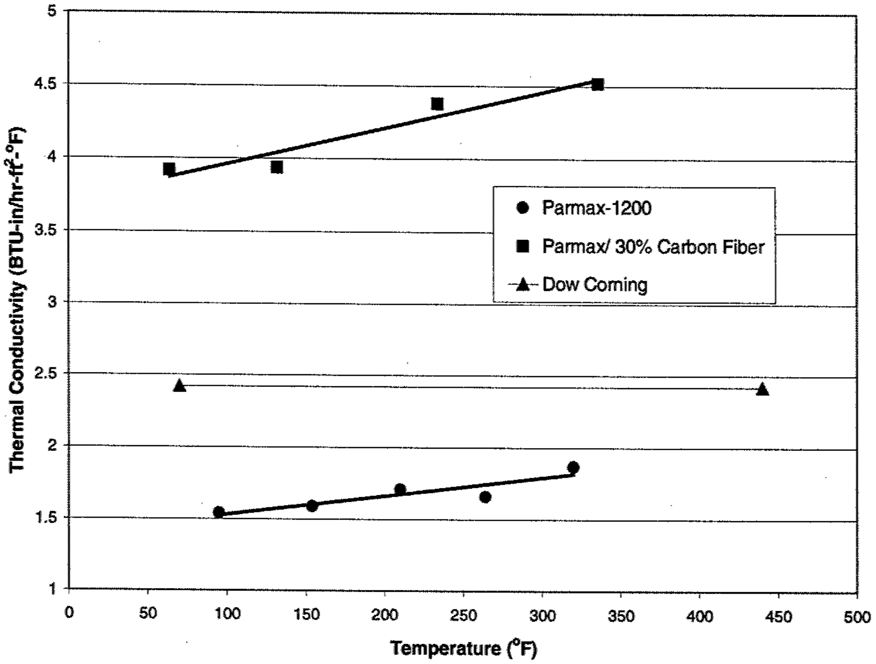


Figure 11. Thermal Conductivity of Parmax® based materials and Dow Corning 93-104

It was obvious that the increased thermal conductivity of the Parmax® SRP materials was due solely to the presence of the carbon fiber. If we could introduce "thermal breaks" into the structure, it was speculated, the overall heat transfer would be reduced significantly. This would be due to the heat transfer now being limited by the substantially smaller thermal conductivity of the pure Parmax® SRP resin.

Thus, we set about fabricating multi-layered samples consisting of Parmax® SRP/CF layers interspersed with pure Parmax® SRP layers. For the purposes of this effort, all specimens were fabricated separately then pressed together to form one specimen. A schematic of this construction is shown in Figure 12. With this construction, the excellent thermo-physical properties of the Parmax® SRP resin compounded with carbon fiber are retained along with creating a thermal break consisting of low thermal conductivity Parmax®-1200 resin to increase the insulative properties of the entire structure.

It is important to note that, owing to the thermoplastic nature of Parmax® SRP resins, the separate layers in combustor insulation can be easily constructed utilizing commercial multilayer co-extrusion technology. To demonstrate the concept, MPT successfully extruded a continuous tube composed of Parmax® SRP resin compounded with 30% carbon fiber as shown in Figure 13.

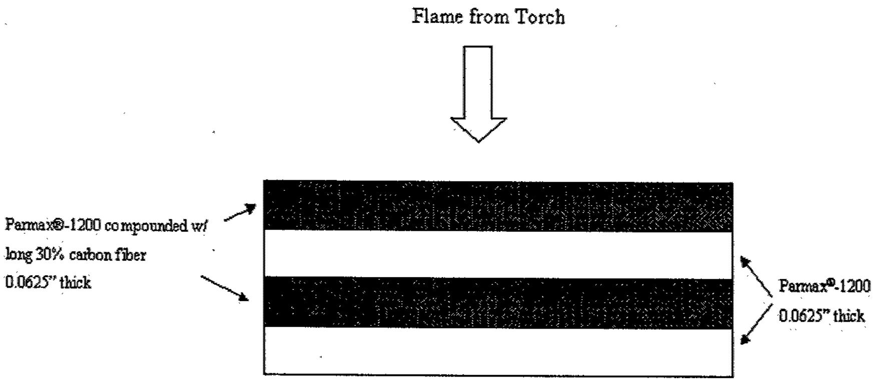


Figure 12. Schematic diagram of multi-layered ablative material construction

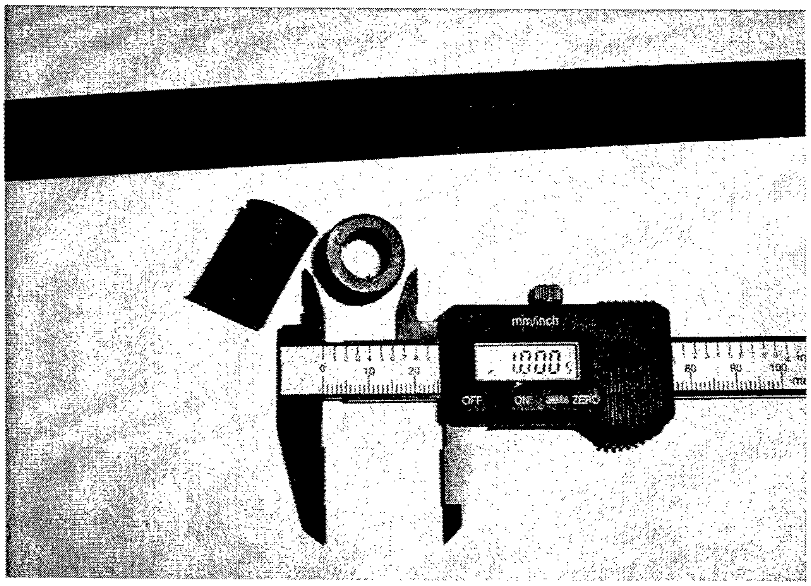


Figure 13. Photo of Extruded Parmax® SRP resin compounded with 30% Carbon Fiber. (Caliper Units in inches)

To prove the concept, the backface temperature of this multi-layered sample was measured and compared against a Parmax® SRP sample compounded with carbon fiber and the Dow Corning material. The data is shown in Figure 14. The thickness of each sample was maintained at 0.25". A custom made sample holder was fabricated for measuring backface temperatures of the samples while eliminating any concerns about flame bleed/wraparound which can introduce significant error into the thermocouple reading.

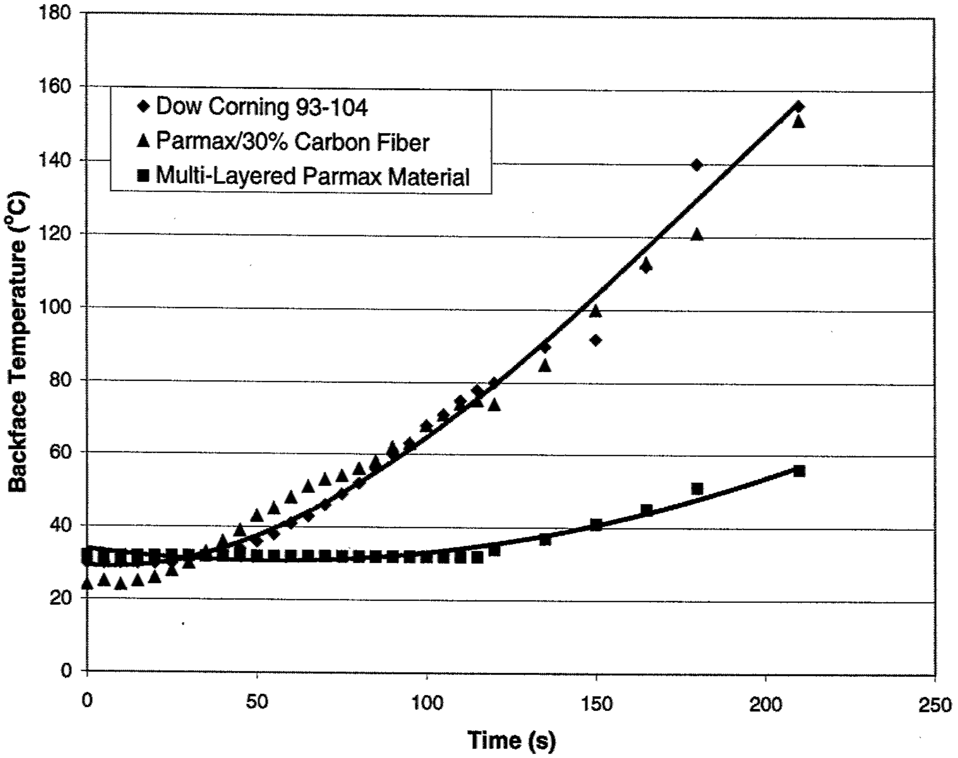


Figure 14. Backface temperature measurements of various ablative materials. Sample thickness: 0.25". Torch distance from sample: 2". 120s burn time.

As can be seen from Figure 14, multi-layer construction dramatically reduces the back side temperatures, richly validating the "thermal break" concept. As a bonus, the reduced density of pure Parmax® SRP results in even lower overall density for the system as a whole (79 lb/ft^3 vs. 84 lb/ft^3 for the compounded material). As expected, the Dow Corning and 30% carbon fiber compounded Parmax materials have equivalent backface temperature profiles.

Summarizing the second portion of this effort, we have successfully eliminated two issues encountered early in the program. We have successfully eliminated the swelling of the Parmax® SRP ablative system and we have dramatically improved insulative properties by utilizing the multi-layered approach. Following these modifications, the assessment of Parmax® SRP resins at this stage in the project is as follows:

- Parmax® SRP formulation have superior erosion performance as per ASTM E285
- Parmax® SRP multi-layered formulation have (an even) lower density (79 lbs/cm^3 vs. 91 lbs/cm^3)
- Parmax® SRP formulation have significantly better insulative performance as measured by backside temperature performance
- Parmax® SRP formulation displayed comparable swelling to Dow Corning 93-104
- Parmax® SRP (at commercial stage) will be lower than or comparable in cost to 93-104

Cost and Fabrication Issues

In the assessment of the Parmax® SRP potential as ablative insulators, we have indicated that cost of Parmax® SRP materials will be lower or comparable in cost to 93-104. The total system cost for any component is based on (at least) 2 factors

- Material Cost
- Fabrication Cost

Material Cost

At present, Parmax® SRPs find themselves in the transition between development and commercial stages. Currently, MPT has pilot plant facilities for production of Parmax® SRP resins with nominal capacity of 100,000 lbs/year. The first commercial plant will have capacity of 1,000,000 lbs/year and is scheduled to come on line in 2005. Consequently, full commercial availability of Parmax® SRP resins is scheduled for mid to late 2005.

The pricing of Parmax® SRPs, as with all polymeric materials, is intimately tied to the production volume. When first commercial grades are introduced (@ 1M lb/year) the pricing will be comparable to 93-104 at $30-35/lb. Thus, from the onset, Parmax® SRPs will be priced comparably to 93-104. Of course, as the production levels ramp up, Parmax® SRP resins will get significantly less expensive (Figure 15), providing for a superior ablative solution at lower cost.

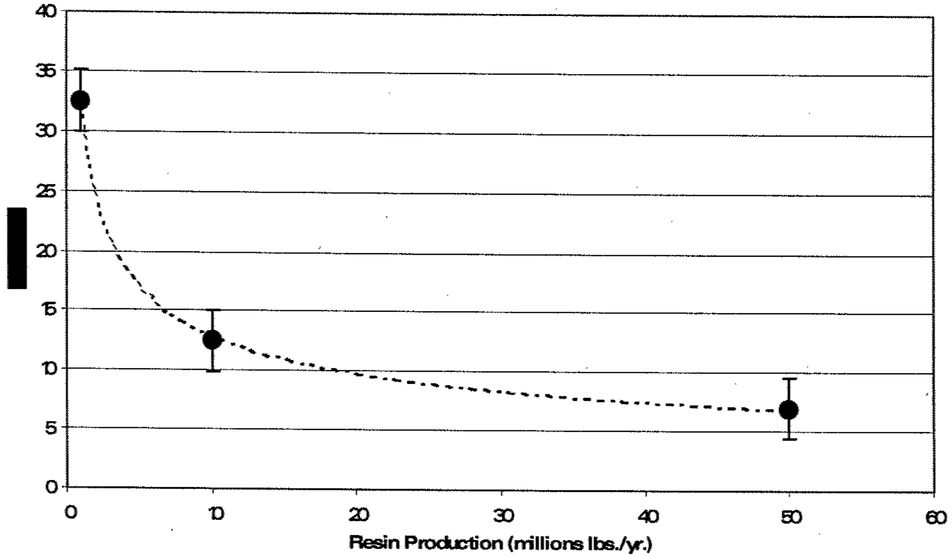


Figure 15. Parmax® SRP resin prices as a function of production volume.

As we can easily see from Figure 15, production levels and pricing are directly dependent on each other. As such, early applications are crucially important for volume increase, which in turn, will bring about the price decrease. It can be reasonably expected that the initial cost (comparable to 93-104) will decrease by about two-thirds.

Fabrication Cost

Obviously, fabrication cost depends on the methodology used. There are a number of options for ramjet combustors that will be addressed in the Phase II effort, with a great deal of input from our partners such as ARC. While MPT is a materials company with expertise in manufacturing components with our materials, our partners will provide an understanding of the unique constraints imposed by this aerospace application. The lowest cost approaches may be high volume mass production methods used globally for thermoplastic fabrication, including extrusion and injection molding. However, the possibility exists for a number of other methods to be used including a lay-up followed by an autoclave step for this particular application.

The lowest cost option will depend upon several factors, such as number of units to be produced, and production process utilized. Regardless of these uncertainties, MPT anticipates that the cost for fabrication will be significantly less or, at worst, roughly the same as that for the existing 93-104 process including the post-cures, etc.

Therefore, MPT is estimating that lightweight Parmax® SRP-based ramjet combustor insulators will potentially offer a cost savings with respect to the existing 93-104 system, in both the material AND fabrication cost.

Collaboration

Collaboration on any Phase II effort is a necessity especially on a subject as complex as rocket engine design. Forming a partnership will ensure that the program is ready to move through the Phase I Option into Phase II without delay. In addition to preparing support for Phase II fabrication, the partner will be valuable in helping to address many of the aerospace technical issues concerning ablative cooling for ramjet combustor engine design.

Presently, MPT has made contact with Atlantic Research Corporation (Gainesville, VA). ARC is anticipated to bring expertise in the design, development and fabrication of air breathing systems. In addition to ARC, MPT will continue to utilize the vast wealth of knowledge and testing methodologies currently in use at the Southern Research Institute.

Conclusions

In the course of performing these tasks we have demonstrated that Parmax® SRP-based ablative systems possess a series of advantages over the existing solution (Dow Corning 93-104) such as:

- Superior erosion rate (< 0.83 mils/sec versus 2.5 mils/sec for 93-104 per ASTM E285)
- Greatly increased insulative properties (18 s/mm insulation index vs. 1 s/mm for 93-104)
- Reduced ablative material density (79 lb/ft^3 vs. 91 lb/ft^3 for 93-104)
- Orders of magnitude greater strength before and after the burn
- Cost-effective processing techniques (extrusion, compression and injection molding)
- Comparable material cost combined with easier processing techniques should result in the lower overall system cost.

Thus, even a simple drop-in replacement of Parmax® SRP ablative system would yield a number of benefits including better ablative performance, lower overall system weight and cheaper system assembly.

Revolutionary advances, however, can be expected once designers take full advantage of the superior properties of the new system. Greatly increased insulative properties of Parmax® SRPs, for example, may lead to increased combustion chamber temperatures, leading to the increased range and/or payload. Alternatively, one could envision reduction in the overall system weight since the thickness of the insulation can be reduced due to the superior erosion rate and heat barrier properties of the improved system.

Finally, by combining the superior ablative and mechanical properties of Parmax® SRPs, it is potentially foreseeable that the entire ramjet combustor could be fabricated out of Parmax® SRPs, eliminating the insulated steel case. This elegant solution would provide tremendous system performance benefits, including increased range/payload, reduced logistical cost due to lighter weight, and potentially reduced lifecycle cost due to elimination of corrosion concerns.

Summarizing, during Phase I we demonstrated the extraordinary promise of Parmax® SRP materials as ablative insulators. In order to successfully transport this fundamental, material science promise into the complex rocket motor system environment, Phase II effort will focus on final material optimization, filling out the gaps in design data and perhaps most importantly, familiarizing the engine designers with the promise of these unique materials.

APPENDIX A – Optimal sample preparation method

The first step in fabricating compounded material was to identify an optimal method, which would properly disperse the additive throughout the polymeric matrix. Two initial compounding methods were investigated: melt mixing and polymer solution blending.

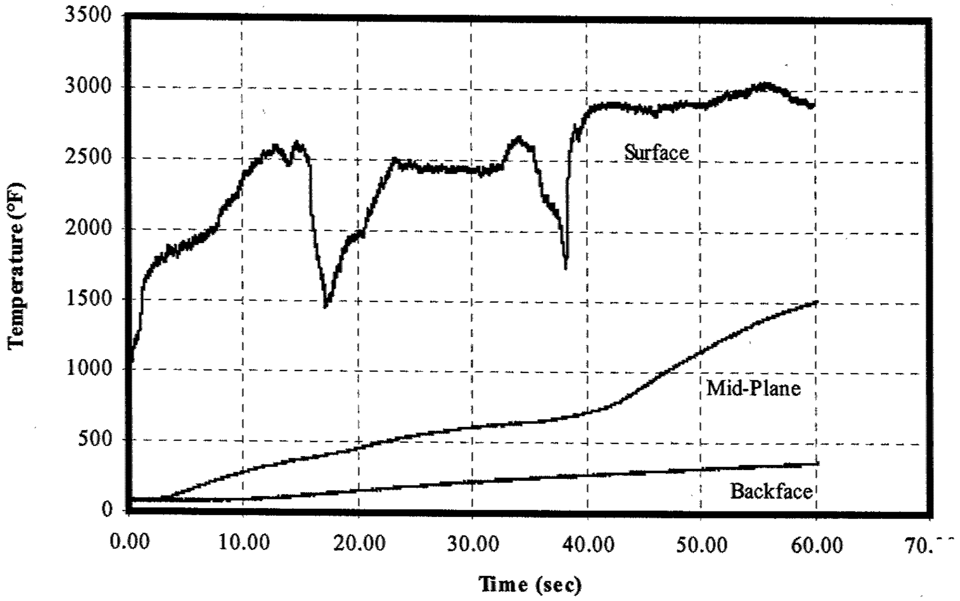
Melt mixing was accomplished by first creating a polymer melt using a laboratory intensive melt kneader (Brabender Plasticorder). Compounding was performed in the processing window of Parmax® SRP resins (280°C to 350°C), with melt feeding of the additives, subsequent to resin classification.

Polymer solution based mixing was achieved by adding the material to a 10% Parmax®/N-methylpyrrilidone (NMP) solution. The mixture was thoroughly blended with a mechanical mixer for 30 minutes before being coagulated in a 5% isopropyl alcohol/water solution. After coagulation, the compounded material was rinsed multiple times with distilled water and dried thoroughly at 177°C in a convection oven.

The compounded material was then compression-molded into plaques using a 30-ton Carver heated laboratory press. The pressing temperature was 315°C (600°F). Mechanical testing was done with a MTS G20 Universal Testing Machine. The samples were tested in a flexural (3-point bending) configuration, allowing for calculation of flexural moduli, strengths and elongations.

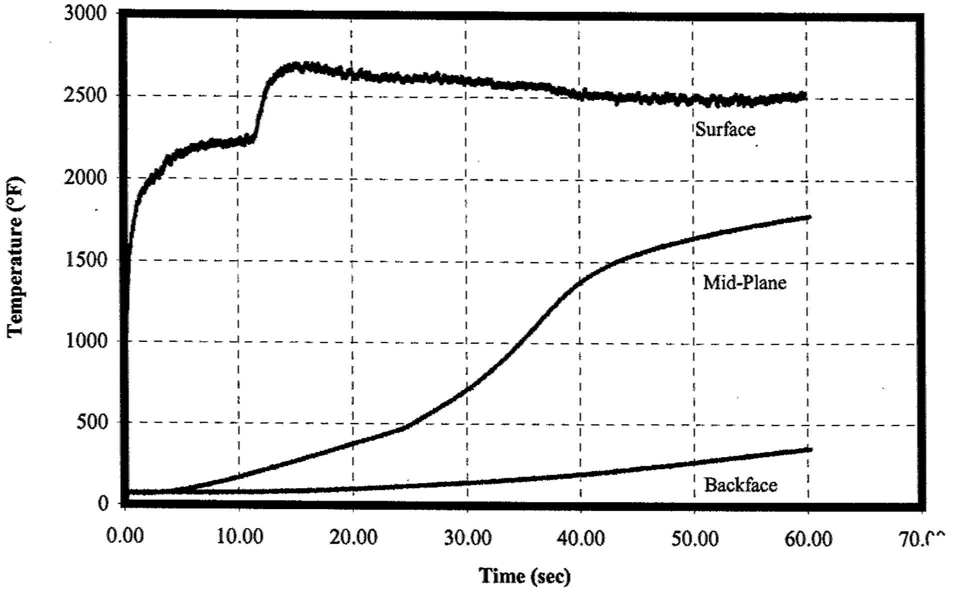
Initial results comparing the two methods strongly suggested that the solution mixing method did a better job of compounding the materials than melt mixing. Solution mixed samples displayed consistently greater mechanical properties along with lower rates of erosion in initial flame impingement tests. This result is attributed to: 1) the ease of mixing additives into a low viscosity polymer solution versus a highly viscous polymer melt and 2) shortening of the effective fiber length during the melt compounding process owing to the high shear environments. The primary concern with using a solution based method is the complete elimination of the flammable solvent. This issue was overcome with proper coagulation, rinsing and drying techniques.

APPENDIX B – Additional laser thermal testing data



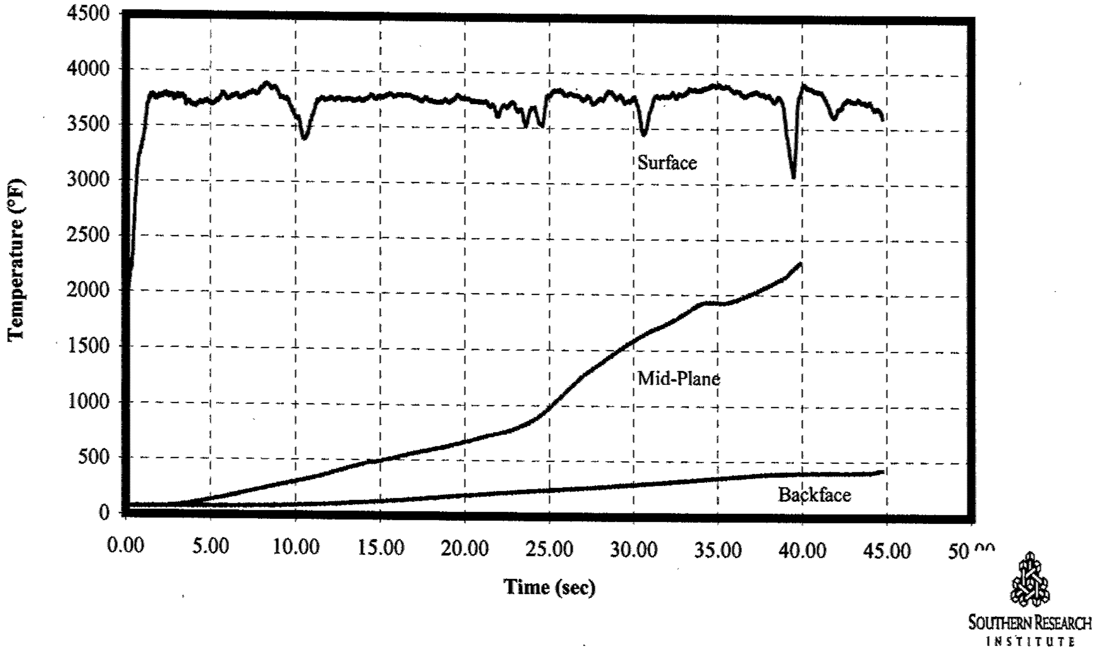
SOUTHERN RESEARCH INSTITUTE

Response of Parmax®/Carbon Fiber Material at 100 W/cm² exposed for 60s. Air Flow: Mach 0.5

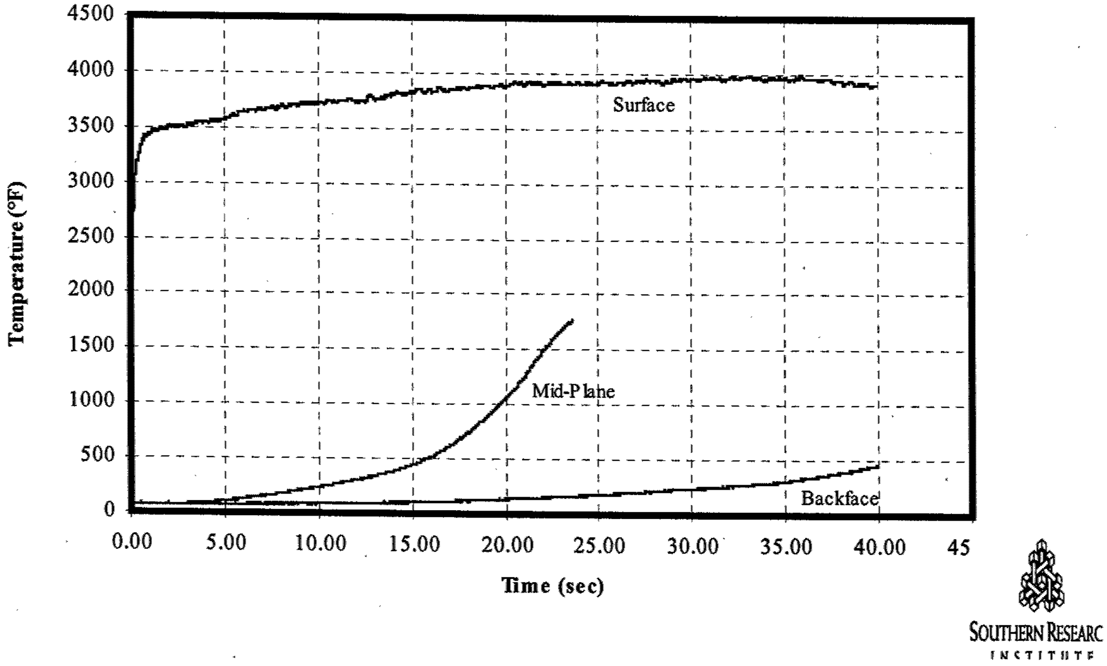


SOUTHERN RESEARCH INSTITUTE

Response of Dow Corning 93-104 at 100 W/cm² exposed for 60s. Air Flow: Mach 0.5.



Response of compounded Parmax® at 300 W/cm² exposed for 45s. Air Flow: Mach 0.5.

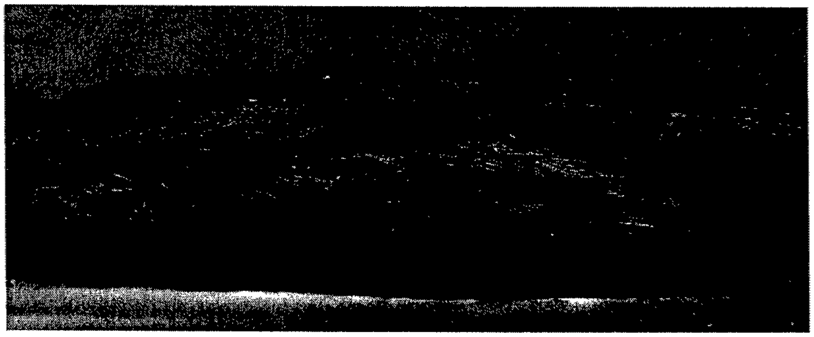


Response of Dow Corning 93-104 at 300 W/cm² exposed for 42s. Air Flow: Mach 0.5.

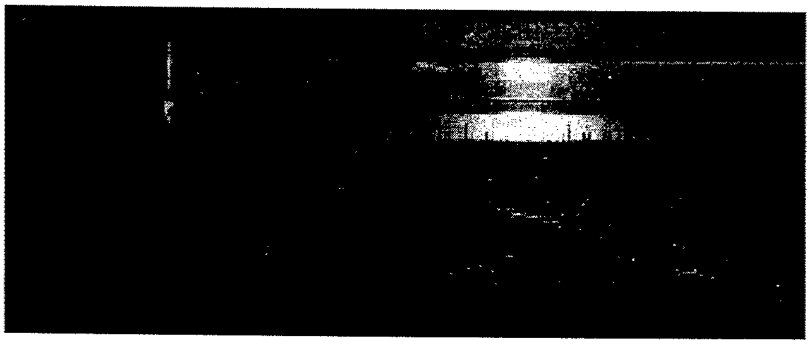
APPENDIX C – Photographs of post-burn samples

Photograph of Dow-Corning 93-104 cross-section
after 120s exposure to a 2500°C oxy-acetylene torch.

Photograph of Parmax® SRP/30% (short) carbon fiber cross-section
after 120s exposure to a 2500°C oxy-acetylene torch.
Sample fabricated with coagulation method.



Photograph of Parmax® SRP/30% (long) carbon fiber cross-section
after 120s exposure to a 2500°C oxy-acetylene torch.
Sample fabricated with coagulation method.



Photograph of multi-layered Parmax® SRP based sample cross-section
after 120s exposure to a 2500°C oxy-acetylene torch.
Sample fabricated with coagulation method.