JOURNAL OF SPACECRAFT AND ROCKETS
Vol. 41, No. 6, November–December 2004

Engineering Notes

ENGINEERING NOTES are short manuscripts describing new developments or important results of a preliminary nature. These Notes cannot exceed six manuscript pages and three figures; a page of text may be substituted for a figure and vice versa. After informal review by the editors, they may be published within a few months of the date of receipt. Style requirements are the same as for regular contributions (see inside back cover).

Development of an Ablative Insulation Material for Ramjet Applications

Gary Beall,* Zahida Shirin,† Stewart Harris,‡
Mickey Wooten,§ and Casey Smith‡
Texas State University at San Marcos,
San Marcos, Texas 78666
and
Alan Bray¶
Systems and Materials Research Corporation,
Spicewood, Texas 78669

Introduction

IT is common practice to utilize various filled composites to protect ramjet combustion chambers from the severe temperatures generated during firings. For example, during firing of a solid rocket motor, internal liners positioned between the case and the propellant are subjected to temperatures in the range of 1000–4000°C with pressures of 1000 psi (6894 kPa) or greater. A current material of choice is Dow Corning (DC) 93-104, a silicone elastomeric material filled with silica and long carbon fibers. It is a trowelable paste and is difficult to cast.[1] DC 93-104 also has a very high density and high thermal conductivity. The density contributes to substantial weight in the rocket, and the thermal conductivity requires thick layers to insulate the ramjet body. This thickness also contributes adversely to ramjet weight. Sanders[2] reported a new silicon-based insulation material, created by mixing two silicon rubber materials DC 93-104 from DC and RTV 615 from General Electric Co. The heat resistance of this material has much higher values than phenolic- and hydroxy-terminated polybutadiene based materials. Polymer nanocomposites have been suggested as ablative and insulative materials in space and launch systems for protection from the severe effects of very high temperatures and incident heating rates. Vaia et al.[3] examined the ablative performance of nylon 6 nanocomposites. A relatively tough, inorganic char forms during the ablation of these nanocomposites, resulting in at least an order-of magnitude decrease in the mass loss rate relative to the neat polymer. This occurs for as little as 2-wt% exfoliated layered silicate. The presence of layers does not alter the first-order decomposition kinetics of the polymer matrix. Instead, the exfoliated silicate layers lead to a uniform char layer that enhances the ablative performance and insulation character. The type of organic modification on the silicate surface only minutely influences the char layer formation. The primary function of the surface treatment is to promote the full dispersion of the nanoparticles into the matrix. Koo et al.[4] explored the ablative and insulative properties of Borden Chemical's SC-1008, a phenolic resin with several nanoparticles such as montmorillonite and carbon fibers. These polymer nanostructured materials showed better performance in erosion rate and heat soaked temperature over MX-4926, which is used in current rocket nozzles. The aim of this work is to study materials that could potentially lower density and heat transfer and improve erosion performance. A silicone was chosen as the base resin, and a variety of fillers were studied. The fillers studied included nanoclays (char formation), diatameceous earth (lower density), zeospheres (lower density), and carbon fiber (ablation resistance).

Experimental

The simulated solid rocket motor (SSRM)[5] facility at Texas State University was used to evaluate the performance of the new materials. The SSRM is a small-scale, liquid-fueled rocket motor burning a mixture of kerosene and oxygen. The SSRM is a controlled laboratory device capable of producing an exhaust environment with measured heat fluxes from 454 to 14,200 kW/m^2. The maximum temperature is approximately 2200°C, and the velocity of the exhaust is approximately 2000 m/s. Calibration of the SSRM was performed using a Medtherm heat flux gauge. The highest heat flux is at 2 in. and the lowest heat flux is at 14 in. from the nozzle exit. The standard sample size is $10 \times 10 \times 1.27$ cm. The ablative samples were bonded to a $10 \times 10 \times 0.32$ cm steel plate. A narrow slot is machined into the bond line side of steel plate for placement of a thermocouple to measure the backside thermal history. C clamps were used to clamp the ablative samples to the steel plate during testing and were placed in a fixture downstream from the SSRM nozzle exit that centers the backside thermocouple with the exhaust from the rocket motor. The fixture has adjustment in axial distance and impingement angle with reference to the exhaust centerline. An axial distance corresponding to 8625 kW/m^2 was used in all experiments. All tests were performed at right angles to the rocket blast for 15 s. Backside temperature rise was recorded as the maximum temperature rise after the rocket motor was turned off. Peak erosion was determined by pre- and posttest measurement using a pencil-point dial indicator. The maximum ablation was measured at the center of the crater relative to an average of five points measured on the surface away from the area affected by the exhaust plume. Mass loss was determined by pre and posttest weight loss measurements. Data sets were averaged from the firing of three samples. The surface temperature of the test samples were measured with an infrared pyrometer focused on the center of the sample. The temperature is recorded at the end of the rocket firing. The data acquired during the experiments included peak erosion, residual mass, maximum backside temperature, time to reach maximum backside temperature, and surface temperature.

Preparation of Samples

The various fillers utilized in this study were mixed with the R2550 silicone resin in two ways. The first method for dispersing the nanoclays involved high shear mixing in a Dispermat mixer

Received 2 April 2004; revision received 12 July 2004; accepted for publication 23 July 2004.

*Assistant Professor, Department of Chemistry and Biology, 601 University Drive.

†Postdoctoral Student, Department of Chemistry and Biology, 601 University Drive.

‡Graduate Student, Department of Chemistry and Biology, 601 University Drive.

§Instrument Technician, Department of Chemistry and Biology, 601 University Drive.

¶President, 19300 Crosswind Circle.

Table 1 Ablative and insulation test results[a]

Sample	Maximum temperature, Δ°C	Time to maximum temperature, min	Peak erosion, in.	Residual mass, %	Density, g/cm^3
DC 93-104	41 (3)	4.0 (2)	0.02 (1)	98.4 (1)	1.32 (1)
DC 93-104, 5% 30B	35 (3)	4.7 (2)	0.02 (1)	98.3 (1)	1.27 (1)
R2550, 5%15A, 40%ZS	31 (2)	4.5 (2)	0.45 (1)	92.2 (4)	1.47 (7)
R2550, 5%15A, 25%DE	32 (3)	3.7 (2)	0.16 (3)	92.8 (6)	1.11 (5)
R2550, 40%ZS, 5%15A, 1%CF	33 (3)	4.2 (2)	0.23 (3)	96.4 (4)	1.32 (2)
R2550, 35%ZS, 5%15A, 2%CF	33 (3)	4.6 (2)	0.11 (3)	97.7 (3)	1.35 (2)
R2550, 30%ZS, 5%15A, 3%CF	31 (3)	5.2 (2)	0.09 (3)	97.8 (3)	1.26 (3)
R2550, 25%DE, 5%15A, 0.5%CF	19 (2)	4.3 (2)	0.53 (3)	87.8 (3)	1.22 (2)
R2550, 25%DE, 5%15A, 1%CF	23 (2)	4.5 (2)	0.43 (2)	94.1 (2)	1.06 (2)
R2550, 20%DE, 5%15A, 1%CF	22 (2)	5.0 (2)	0.33 (2)	95.9 (2)	0.99 (2)
R2550, 10%DE, 5%15A, 3%CF	39 (3)	5.7 (2)	0.05 (2)	97.6 (2)	0.94 (2)

[a]Numbers in parentheses are standard deviations.

equipped with a Cowles mixing blade at 2000 rpm for 5 min. The other fillers were then mixed in with the resin with low shear mixing in a Kitchen Aid bowl mixer for 10 min. Table 1 is a compilation of the various mixtures produced for testing. The various mixtures were cast into wooden molds lined with polyvinylidene chloride film. These samples were heated in a vacuum oven at 75°C for 10 min to degas the samples and then placed in a conventional oven at 75°C for two days to cure. Samples of the DC 93-104 were cast in the same molds following the manufacturer's recommendations as comparative standards.

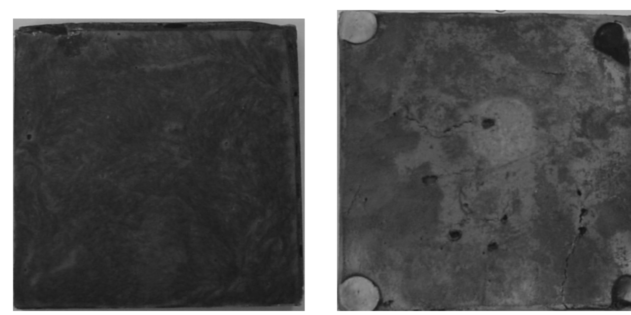
Materials

The following sources were utilized for the filler materials utilized in the study: Cloisite 15A and 30B (Southern Clay Products), Zeospheres (3M Corp.), diatomaceous earth (Best Prices Storable Foods), and chopped carbon fiber (AS4BLC 12K from Hexcel Carbon Fibers). The R2550 silicone resin was purchased from NuSil Corp. and the DC 93-104 from DC.

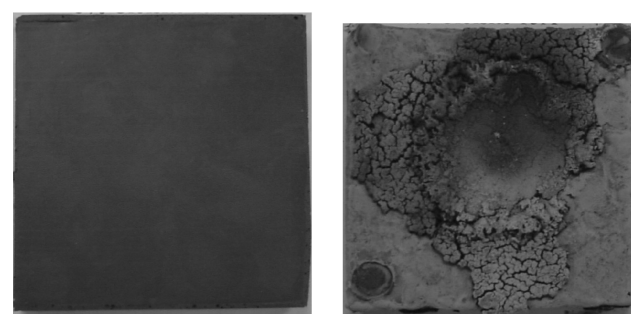
Results and Discussion

Table 1 contains the composition and SSRM data for all of the plaques tested. The DC 93-104 material yielded an average mass loss of 1.6 ± 0.1%, a peak erosion of 0.02 ± 0.01 in., and a maximum backside temperature rise of 41 ± 3°C. A simple addition of organoclays to the DC was made to determine if the insulative character could be improved. The performance of the DC with the addition of 5% organoclays did not perform much differently, with only a 6°C lower maximum heat rise. This performance can be attributed to the extreme high viscosity of the DC, which precludes high shear mixing that is critical to dispersion of the nanoclay and subsequent ablation performance. The filled R-2550 composite samples performed slightly better on lowering the maximum heat rise with Zeopheres (ZS) averaging a 31 ± 2°C rise and diatomaceous earth (DE) averaging 32 ± 3°C. This may be because the nanoclays could be incorporated into the resin under high shear conditions. The nanoclays were still mainly in an intercalated state rather than fully exfoliated as indicated by x-ray diffraction. The compatibility of the nanoclays can be substantially improved to yield better exfoliation; however, this work was limited to commercially available organoclays.

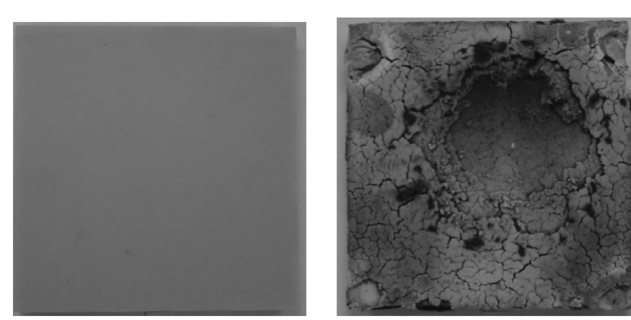
The results of the first round showed significant insulation improvement over DC for the filled nanocomposites. The sample containing 40% ZS exhibited a 24% reduction in backside temperature and the sample containing 25% DE had a 22% reduction. This is exactly what has been seen in other nanocomposites where the char layer formed by the nanoparticles forms an insulating layer. The goal of lowering density was fulfilled by the DE sample with a 16% reduction in density. The sample containing ZS was actually higher in density relative to DC. The ablative properties, particularly erosion, however, were much worse than DC, yielding unacceptable levels of ablation. The test specimens before and after SSRM testing are shown in Fig. 1. In the case of DC, the tested sample has a small shallow crater approximately 1 in. in diameter. A cross section of one of the samples showed a burn out layer of 0.123 in. in thickness. The sample R2550 40% ZS 5% Cloisite 15A (15A) has a fairly deep crater approximately 2 in. in diameter. The char or burned out layer has been completely eroded away within the crater and much of the char layer around the periphery has scaled off. The char layer that was not ablated is quite clear in Fig. 1.



a) DC 93-104



b) R2550 + 40% ZS + 5% Cloisite 15A



c) R2550 + 25% DE + 5% Cloisite 15A

Fig. 1 Selected ablative test samples before (left) and after (right) testing.

The R2550 25% DE and 5% Cloisite 15A sample also exhibited a large crater of approximate $2\frac{1}{2}$ in. in diameter. As in the preceding sample, the char layer was completely ablated away within the crater. The char layer on the periphery was a bit less fragile and survived mostly in place on removal from the sample holder. Cross sections of the char layers on the two later samples were slightly smaller than DC at 0.1 in. Observation of the test specimens during the rocket motor firing indicated that the char layer was physically being blown away during the firing. With the amount of material that was ablated in the R2550 series of samples, the lowest backside temperature recorded by the thermocouple could be due to the insulative character of the composite but also could be due to the heat carried away by the ablated material. Without improving the ablative character of the samples, the relative contribution of each factor cannot be determined.

In subsequent rounds of testing, aimed at improving ablative resistance, filler and carbon fiber loading were varied holding the nanoclay content constant. The chopped carbon fibers were added to reinforce the char. Fiber lengths were chosen to be nominally $\frac{1}{4}$ in. Keeping fiber length short has a significant advantage in the casting process because very long fibers interfere with the pumpability of the uncured composites.

Effect of Long Carbon Fiber

The best ablative performance for ZS-filled samples was found for the lowest loading of 30% with peak erosion of 0.09 ± 0.03 in. and total mass loss of 2.2%. The unfortunate result for the best performing ZS samples is that no advantage was observed over DC in density. The trends observed for the DE-filled samples yielded much larger effects due to filler loading. The best thermal performance was seen at a loading of 25% DE and yielded a maximum temperature rise of $19 \pm 2°C$, which is a 54% improvement over the DC. The ablative character of this sample was quite poor with a 12.2% mass loss. The same formula with 1% carbon improved the ablative character to a mass loss of 5.9% without an increase in maximum heat rise.

A further improvement in ablative character without loss of insulative character was obtained by lowering the DE from 25 to 20%. This sample yielded a mass loss of 4.0% and a large improvement of peak erosion. Further increase in carbon fiber and removal of DE yielded further improvements in ablative character, a maximum mass loss of 2.44% and peak erosion of 0.05 ± 0.02 in. The density of the last two samples is 0.987 and 0.945 g/ml. Figure 2 shows the improved ablative character gained by inclusion of carbon fiber and the insulating effects of the various fillers. Increasing carbon fiber content improves erosion performance. Table 1 shows the ablative and insulation results of all rounds of testing. Figure 3 shows photographs of samples with different levels of carbon fibers. The effect on the ablative character of the samples is striking. In the sample containing 0.5% carbon fiber, it is clear that substantial amounts of the char has been blown off the sample and there is a deep crater. In the second sample containing 1% carbon fiber, much less of the char layer is gone and the crater is reduced substantially. In the third sample, containing 3% carbon fiber, the insulative layer is almost completely intact and the crater is quite shallow. The char layer when measured in cross section is 0.09 in. at the thickest point, which is substantially smaller than that observed for DC. This is indicative of the higher insulative character of the char layer.

The heating curves for the round two data are shown in Fig. 4. These curves indicate the clear thermal insulation advantage the R2550 formulated with DE/ZS and 15A have over the DC material. For the series of samples filled with ZS, the best insulation was a maximum temperature rise of $31 \pm 3°C$, a 24% improvement over DC. The level of ZS varied from 30 to 40% and did not affect the maximum temperature rise significantly.

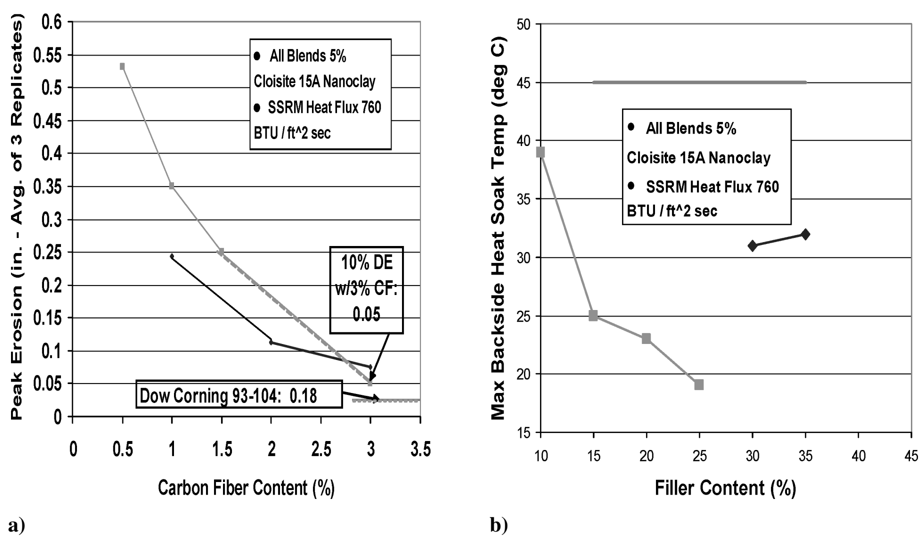
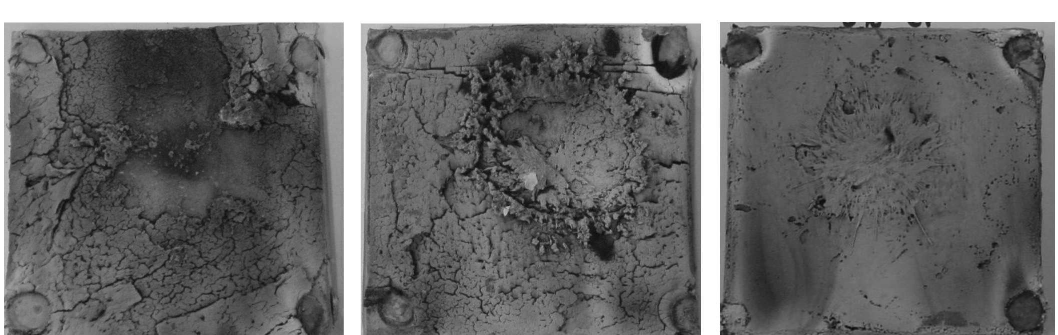


Fig. 2 Summary of erosion and backside temperature data: a) ♦, ZS (40, 35, 30%) and ■, DE (25, 20, 15, 10%); and b) ♦, ZS; ■, DE; and ——, DC 93-104.



a) 0.5% Carbon fiber **b) 1.0% Carbon fiber** **c) 3.0% Carbon fiber**

Fig. 3 Effect of carbon fiber loading on ablation for R-2550 filled with 5% Cloisite.

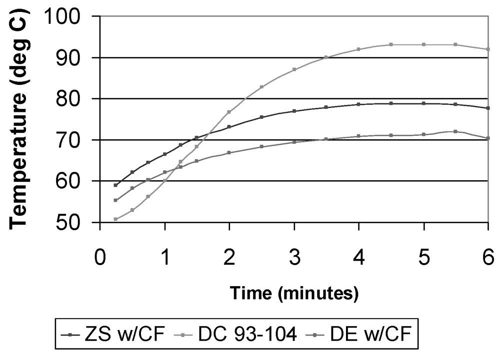


Fig. 4 Heating curves for SSRM tests.

Conclusions

It appears that an optimum ablative composite can be obtained by variation of DE, nanoclay, and carbon fiber to gain the best balance of the objectives of low heat transfer, resistance to ablation, and lower density. It is clear that the objective of lower heat transfer and lower density have been demonstrated. Ablative resistance has been shown to approach that of DC, and trends using carbon fiber in combination with DE would indicate that it could be surpassed. The improvements seen in heat transfer and density could lead to substantial weight savings in the ramjet motor. The new formulations are much easier to process and would potentially improve production throughput and reduce cost.

Acknowledgments

We thank the U.S. Navy for their support of Small Business Innovative Research Topic N02-165 and Southern Clay Products for supplying nanoclays used in this study.

References

[1]"DC 93-104 Material Data Sheet," Dow Corning Corp., Midland, MI, Sept. 2002.

[2]Sanden, R., "Castable Silicone Based Heat Insulation for Jet Engines," *Polymer Testing*, Vol. 21, No. 1, 2001, pp. 61–64.

[3]Vaia, R. A., Price, G., Ruth, P. N., Nguyen, H. T., and Lichtenhan, J., "Polymer/Layered Silicate Nanocomposite as High Performance Ablative Materials," *Applied Clay Science*, Vol. 15, No. 1–2, 1999, pp. 67–92.

[4]Koo, J. H., Stretz, H., Bray, A., Weispfenning, J., Luo, Z. P., Blanski, R., and Ruth, R., "Nanocomposite Rocket Ablative Materials Characterization and Performance," AIAA Paper 2003-1769, April 2003.

[5]Koo, J. H., Kneer, M., Chaboki, A., and Schneider, M., "A Cost-Effective Approach to Evaluate High-Temperature Ablatives for Military Applications," *Naval Engineers Journals*, Vol. 104, No. 3, 1992, pp. 166–177.

T. Lin
Associate Editor