Development of New Thermal Protection Systems Based on Silica/Polysiloxane Composites: Properties Characterization II

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ABSTRACT

This research is the second installment of an effort to characterize a new ablative material through a collaboration between The University of Texas at Austin and Dyna-Glas, LLC. The DG-UHTR polysiloxane resin system manufactured by Dyna-Glas, based on a blend of polysiloxane chemistries, was compared to SC-1008 phenolic resin and evaluated in terms of combustion, flammability, and ablation properties. DG-UHTR was used to fabricate silica fiber-reinforced composite materials by compression molding of prepreg. The silica/DG-UHTR was compared to silica/phenolic fiber-reinforced polymers (FRPs) made in our lab as well as silica/phenolic prepreg purchased commercially. The neat DG-UHTR polysiloxane resin showed a high char yield at 86.5% than the neat SC-1008 resin at 55.4%. Composites made from the DG-UHTR resin showed exceptionally high char yields of 97.5%, 96.7%, and 95.8% for 35wt%, 40wt%, and 48wt% samples. The composites showed superior recession rate, peak heat soak temperature, mass loss rate, and mass loss percent during ablation testing using an oxy-acetylene test bed (OTB).

1. INTRODUCTION

Ablative materials manufactured mainly by the aerospace and defense industries help protect key structures by acting as a sacrificial protective layer. An ablator, in general terms, is a material that dissipates heat by thermochemical degradation. Ablatives are typically bonded to metal substrates using adhesives, so it's essential for the ablative to have good insulative property, so the adhesive will not fail prematurely causing catastrophic failure. There are various mechanisms than can prevent the intensive heat from reaching the backside of the ablative. Strong endothermic reactions help absorb heat as the material degrades and cooling pyrolysis gases diffuse through the porous char layer. The charred layer formed after thermal degradation also acts as a protective barrier, preventing direct flame contact with the virgin ablative material and providing an additional layer of insulation.

One of the most prevalent resins used for such applications is SC-1008 phenolic resin. The relatively low cost and the extensive characterization of the resin makes it an attractive choice for high temperature composite materials. Other high temperature resins have begun to gain traction in the industry, such as cyanate ester, which was used in the composite compression pads as part of Orion's TPS [1].

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The aim of this study is better characterization of the polysiloxane based DG-UHTR resin manufactured by Dyna-Glas, LLC. Previous research from the Koo Research Group (KRG) has identified several advantages of the neat resin system showing its exceptional char yield, thermal stability, and flammability properties [2]. Because of the char's role in an ablative effectiveness, it was hypothesized that the high char yield of the DG-UHTR resin would enhance the protective mechanism, making it a desirable ablative material. Fiber Reinforced Polymers (FRP) were created using high grade silica fabric and DG-UHTR resin, and then compared to a commercially made MX2600 S/Ph composite [3]. It was found that the S/DG-UHTR composites exhibited lower material recession, lower backside temperature, and lower mass loss when compared with the MX2600 S/Ph ablative. The current research is a continuation of the properties characterization of the ablative FRPs, focusing on the ablation mechanism.

2. MATERIAL SYSTEMS

2.1 Resin System Characterization and Properties Characterization I

Previous research examined properties of the neat DG-UHTR resin compared to other commercially available high temperature resins [2]. Neat SC-1008 phenolic resin, made by Hexion, was used as the control sample. This MIL-standard resin is widely used in ablative FRPs utilizing silica and carbon fiber as reinforcement [4]. The resin was also compared to PT-15 cyanate ester, which is manufactured by Lonza [5].

DG-UHTR is formulated using a proprietary (patent pending), inorganic matrix of a variety of polysiloxane chemistries. It is a resin system tailored to produce TPS laminates [9]. Dyna-Glas, LLC is the manufacturer and recently introduced a series of ceramic matrices specifically designed as binders for composite material as flame shielding barriers [6].

Thermal combustion and flammability properties were obtained using a Govmark MCC 2 in accordance with ASTM D7309-2007. Each of the three resins were tested three times using the MCC. The pyrolyzer was heated from 100°C to 750°C at a rate of 1°C/sec, while the temperature of the pyrolyzer was held at 900°C.

As seen in Figure 1, it was observed that the DG-UHTR polysiloxane had the lowest peak heat release rate (HRR) at 630°C and lowest heat release capacity (HRC) with value of 36 J/g-K. PT-15 cyanate ester was found to have large peak heat release rate at 456°C the highest HRC of 159.3J/g-K. SC-1008 phenolic was observed to have a multiple HRR peaks, with a HRC of 53.3J/g-K.

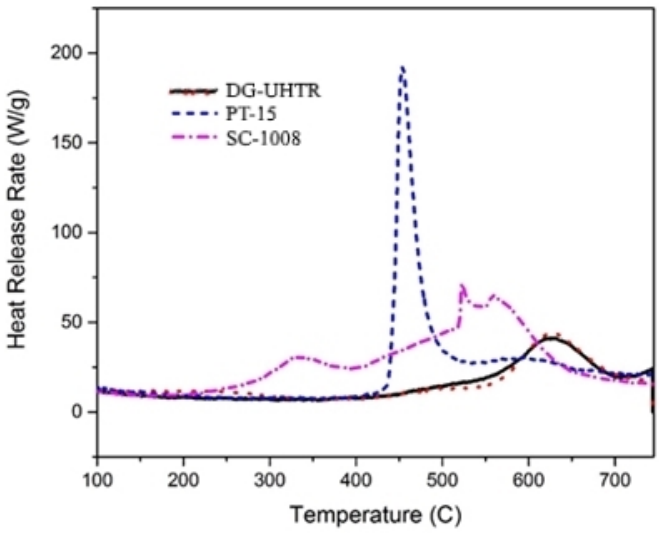


Figure 1. Heat release curves for the several high temperature resin systems [2].

A TA Instruments Hi-Res TGA 2950 Thermogravimetric Analyzer (TGA) was used to examine the thermal stability of the cured resin samples. A procedure for testing samples using TGA, developed by NASA, was adopted to better compare the various materials [7]. Each sample consisted of a 20-mg piece, which was dried at 150ºC for 30 minutes. Then the sample was held at a constant heating rate of 20ºC/min until it reached 1,000ºC. To prevent oxidative degradation, all heating was done in a nitrogen atmosphere. This definition to determine char yield was repeated throughout TGA testing for new data presented later in this paper.

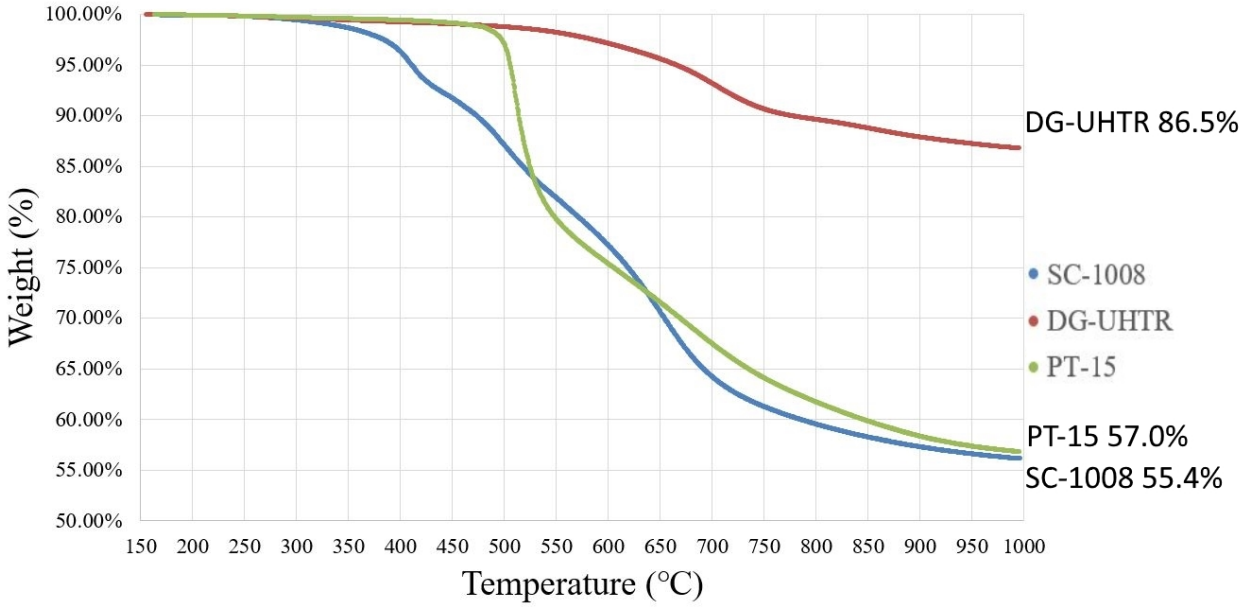


Figure 2. TGA curves for the three neat resin systems [2].

As seen in Figure 2, the DG-UHTR resin showed a high char yield of 86.5%. This was observed to be much higher than the 57% char yield of the PT-15 cyanate ester and 55.4% of the SC-1008 phenolic. Figure 3 shows the derivative of TGA curve in Figure 2, which can be used to show at what temperature regions chemical degradation reactions are occurring. SC-1008 phenolic showed three distinct chemical reactions at 410ºC, 511ºC, and 655ºC. PT-15 cyanate ester showed one sharp peak at 512ºC. The DG-UHTR resin showed one distinct peak at 722ºC and another minor peak at 873ºC. The data indicate that the DG-UHTG resin has the highest decomposition temperature (722ºC) as compared to both SC-1008 (410ºC) and PT-15 (512ºC).

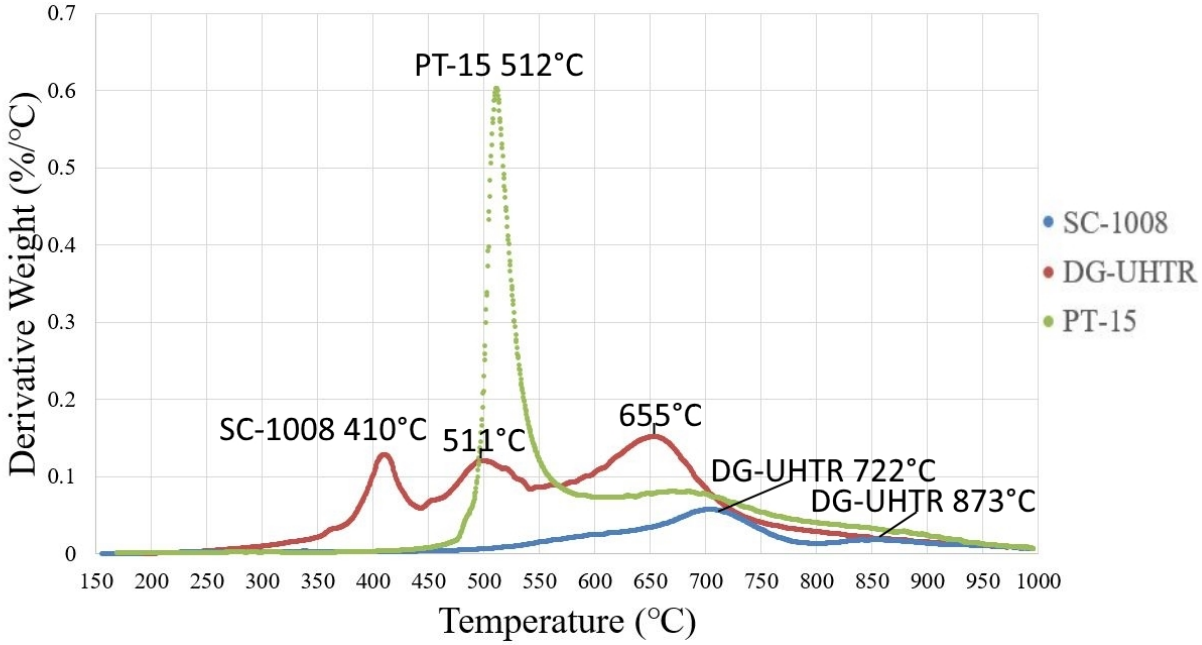


Figure 3. dTGA curves for the three neat resin systems [2].

2.2 Sample Manufacturing

The SC-1008 phenolic resin in an IPA solvent was obtained courtesy of Mektech Composites Inc. S/Ph prepreg was prepared by using the wet lay-up method to distribute the resin evenly across the 99% SiO_2 silica fabric purchased from Cytec, which had a nominal weight of 19 oz/yd^2. The resulting wet lay-up was then placed in a vacuum oven, where it was heated at a rate of 1°C/min, from room temperature to 80°C, and held for 1 hr. Then it was slowly heated to 90°C where it was held for 3 hr, and subsequently heated to 95°C and held for 3 hr. The resulting prepreg was then cut into ½" x ½" squares and compression molded at 150°C in a closed mold, with venting for gases produced during curing to escape. The sample was pressed at 1,000 psi for 5 min, 4,000 psi for 10 min, and then 8,500 psi for 150 min. The sample was then allowed to cool to room temperature under pressure. F0 was produced at 39wt% resin. In a recent study, a piece of MX2600, which contains 30-34% resin, 64% fiber, and 4.5% silica powder, was purchased from Cytec and used as a control material [8].

The DG-UHTR resin was provided by Dyna-Glas, LLC and consisted of 35wt% IPA as the solvent. The resin processed in a similar manner as the S/Ph prepreg. The resin was distributed on the fiber via wet lay-up and vacuum impregnated into aerospace grade silica fabric. The prepreg was made by curing the impregnated fiber at 80ºC for 5 hr under a 5 psi vacuum, and subsequently

heating at 120°C for 5 hr, with all heating rates at 1ºC/min. Once chopped into the same size squares as the S/Ph, the S/DG-UHTR prepreg was compression molded at 2,000 psi for 120 min at 265ºC. The mold was modified with O-rings to help prevent the low viscosity resin from flowing out of the mold, allowing greater control to hit the target resin content. Three samples, containing 35wt%, 40wt%, and 45wt% resin, designated as F1, F2, and F3, respectively, were processed and partially evaluated in a previous study [3].

2.3 Oxy-Acetylene Test Bed

To evaluate the ablative performance of the samples, an oxy-acetylene test bed (OTB) was used to simulate high heat flux conditions experienced by ablatives. A neutral 1.1:1 oxygen to fuel ratio was supplied to a #4 victor welding tip. A Vatell Gardon heat flux transducer (Thermogage 1000-54) was used to correlate the heat flux of the resulting flame to the distance from the torch tip. The samples were exposed to a heat flux of 1,000 W/cm^2 for 40s at a neutral oxy-acetylene flame.

Six 15.5 mm diameter cylindrical samples for each different material were machined via waterjet from the compression molded samples. A miniature 0.55 mm diameter type-K shielded thermocouple (TC) was inserted in the backside of each sample, such that the probe of the TC was 10 mm from the surface exposed to the flame. A LumaSense Technologies ISQ5 two-color IR pyrometer, M9104 Mikron IR video camera and DALSA DS-21-04m12-12e HD video camera focused on the front surface of the sample.

Figure 4. Overview of the ablative testing setup [3].

3. DISCUSSION OF RESULTS

3.1 Thermal Stability Testing Results

Each FRP formulation was evaluated for thermal stability using the same char yield definition used in a previous study [2, 7]. As seen in Figure 5, the char yield for all materials increased significantly

with the inclusion of silica fiber. The F1 formulation, containing 35wt% DG-UHTR resin, showed the highest char yield with 97.5%. The F2 and F3 formulations showed char yields of 96.7% and 95.8%, respectively. This shows an expected trend of a lower the char yield at higher resin content since the silica fiber can withstand temperatures much higher than 1,000ºC. An interesting phenomenon observed is that after 850ºC, it appears the S/DG formulations begin to slightly increase in mass. This may be indicative of some sort of unknown reaction happening on the surface of the char.

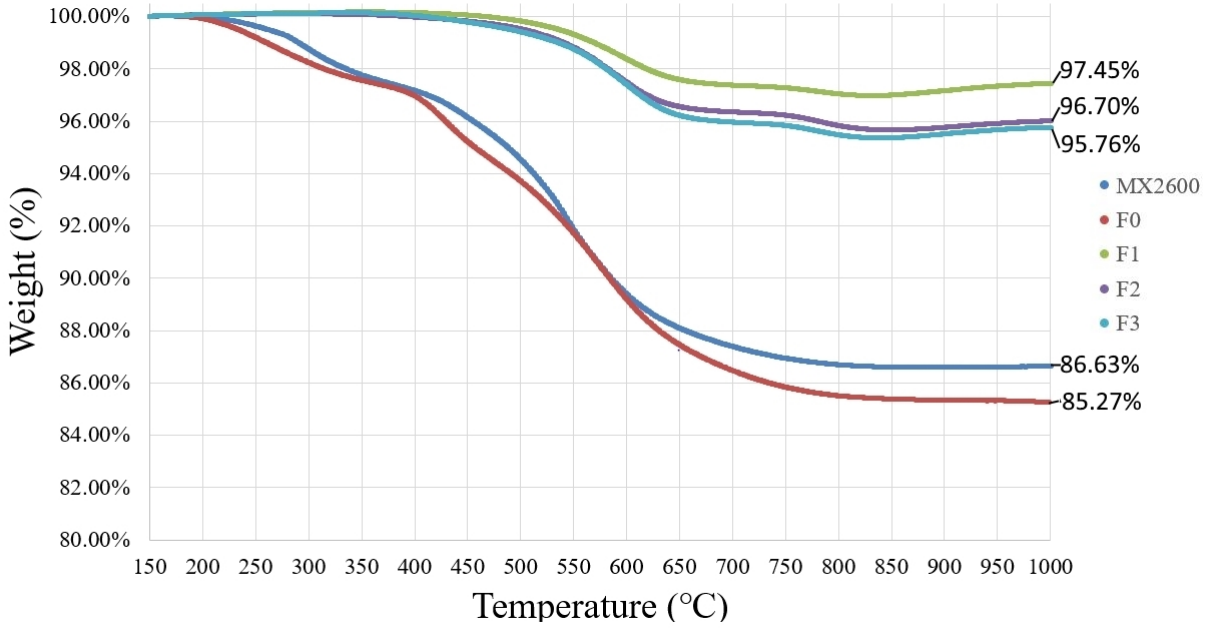


Figure 5. TGA curves for the FRP ablatives.

The 40wt% phenolic resin sample, F0, showed the lowest char yield, with 85.3% of the mass remaining. The commercially bought MX2600 showed a slightly higher char yield of 86.6%. This can be attributed to the fact that the MX2600 contained an estimated 30-34wt% phenolic resin, which would cause it to lose less mass during the degradation. It also contains up to 4.5% silica filler, which may account for both the increased char yield, and the difference in the TGA curve seen from the 200ºC to 550ºC range. It appears the MX2600 has better thermal stability between these temperatures, and does not contain the sharper drop in mass observed at 250ºC and 400ºC.

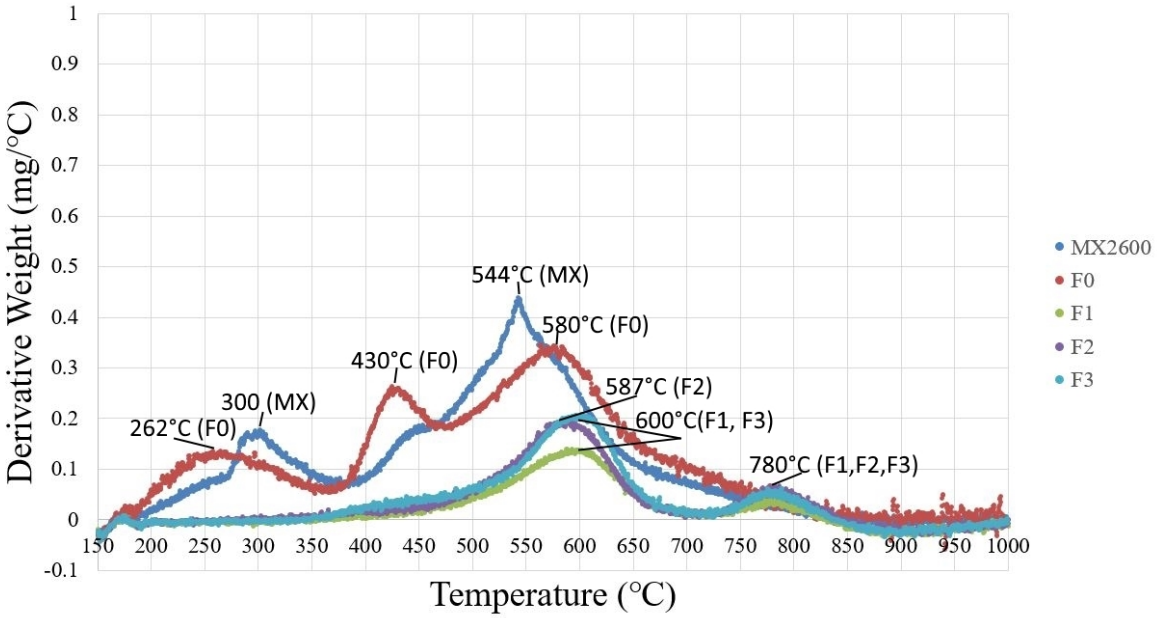


Figure 6. dTGA curves for the five FRP ablatives.

Figure 6 shows the derivative of the TGA curves for the FRPs, and helps highlight some of the differences in the composites at the state of thermal degradation. The F0 sample showed three distinct peaks at 262ºC, 430ºC, and 580ºC. These three peaks tended to happen at lower temperatures compared to the neat SC-1008 resin, which showed three degradation reactions are occurring at 410ºC, 511ºC, and 655ºC in Figure 3. Interestingly, the first two degradation reactions of the F0 appear to happen before the first peak shown for the MX2600, which occurred at 300ºC. The 2nd peak for the MX2600 appears to blend in with the 3rd peak, which happens at 544ºC. This may be due to the silica filler, which is less likely to degrade before the phenolic resin, is helping the FRP to maintain more of its mass during the degradation process occurring at these temperatures. The third F0 peak, occurring at 580ºC, which is 36ºC higher than the third peak in the MX2600.

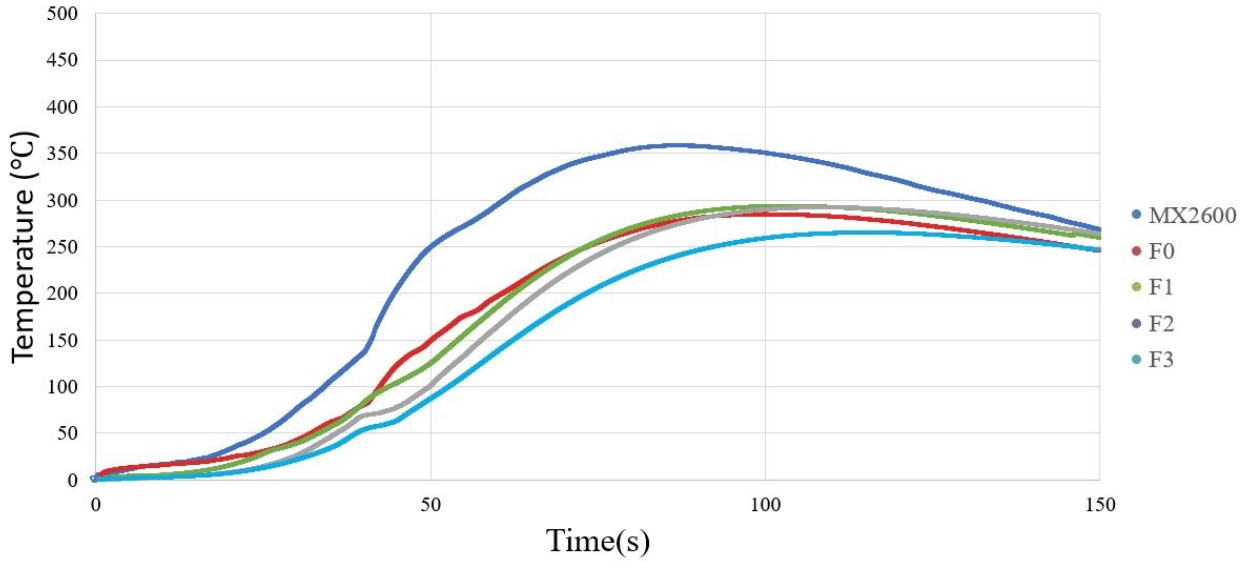
The dTGA graphs for the S/DG-UHTR composites show a similar trend seen in the phenolic samples, where the degradation peaks of the neat resin, illustrated in Figure 3 happen at much lower temperatures. Where the peaks in the neat resin wasn't observed until around 722ºC and 873ºC, the DG-UHTR FRP's peak was observed around 600ºC and 780ºC. The F2 formulation shows a slightly earlier first degradation reaction at around 587ºC, compared to the 600ºC seen for F1 and F3. All three formulations show a 2nd minor peak occurring around 780ºC.

3.2 Ablation Testing Results

The S/Ph F0 sample was evaluated and compared to OTB data which was collected in a previous study [3]. Figure 7 shows a representative temperature vs. time curve measured by the thermocouple. The change in temperature of F0 increases more slowly than the MX2600 samples but slower compared to the S/DG-UHTR formulations. There was very little difference between the S/DG-UHTR formulations in terms of peak heat soak temperature (PHST).

The MX2600 S/Ph sample was found to have an average PHST of 360ºC ± 18, this also had the most variation between the each of the temperature for time curves. The F0 S/PH sample was observed to have a lower PHST, with 290ºC ± 9. This may be due to the fact that F0 had a higher resin content or did not contain the silica filler.

F1 and F2 were seen to have similar PHST values of 290ºC ± 9 and 291ºC ± 4. The F3 S/DG-UHTR formulation had the lowest PHST with an average of 265ºC ± 10 from five samples, as an



outlier was removed. The DG-UHTR shows a trend that higher resin content leads to a lower PHST.

Figure 7. Average temperature vs. time curve for each formulation.

The two-color IR pyrometer measured the surface temperatuer of a small point on the surface of the test sample. Figure 8 shows the 1,800ºC to 2,200ºC region, where it was observed that overall, each sample had very similar surface temperatures of around 2,050ºC. The F0 and MX2600 S/Ph samples both appeared to have most consistent surface temperatures, while the S/DG-UHTR formulations showing greater variability with more peaks and valleys in the curves. A pervious study using IR video cameras revealed that unlike the S/Ph samples, during the ablation process of the DG-UHTR sample tended to have changing regions that would heat up to 2,150ºC and then cool to 2,000ºC, possibly due to the removal of the ceramic char layer that formed during ablation [3]. The IR video of F0 and MX2600 samples both showed a more uniform surface temperature across the face of the sample.

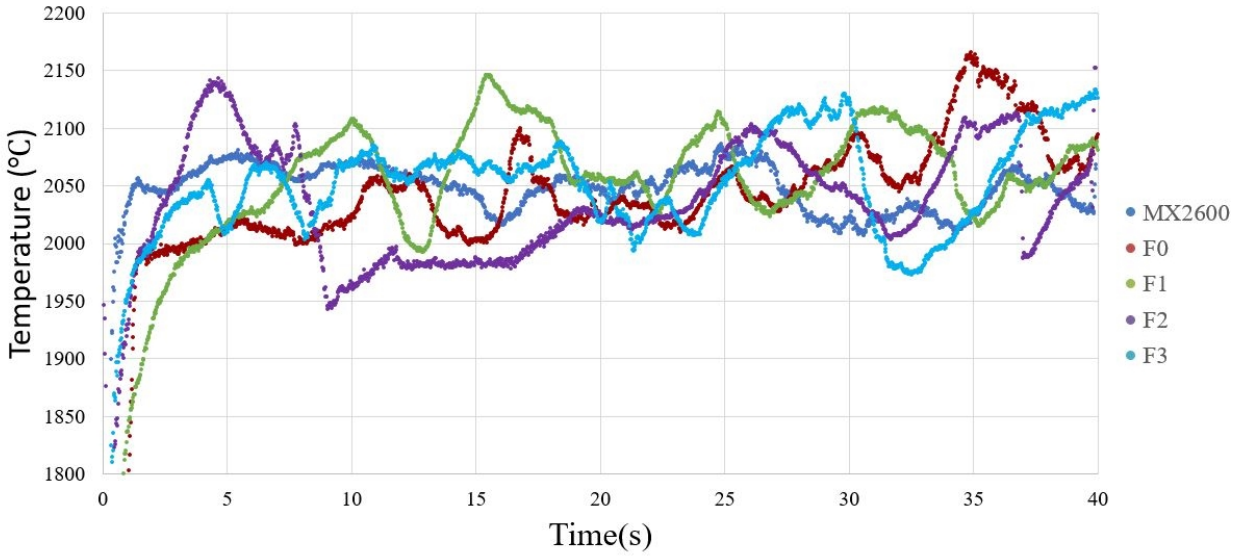


Figure 8. Representative surface temperature measurements.

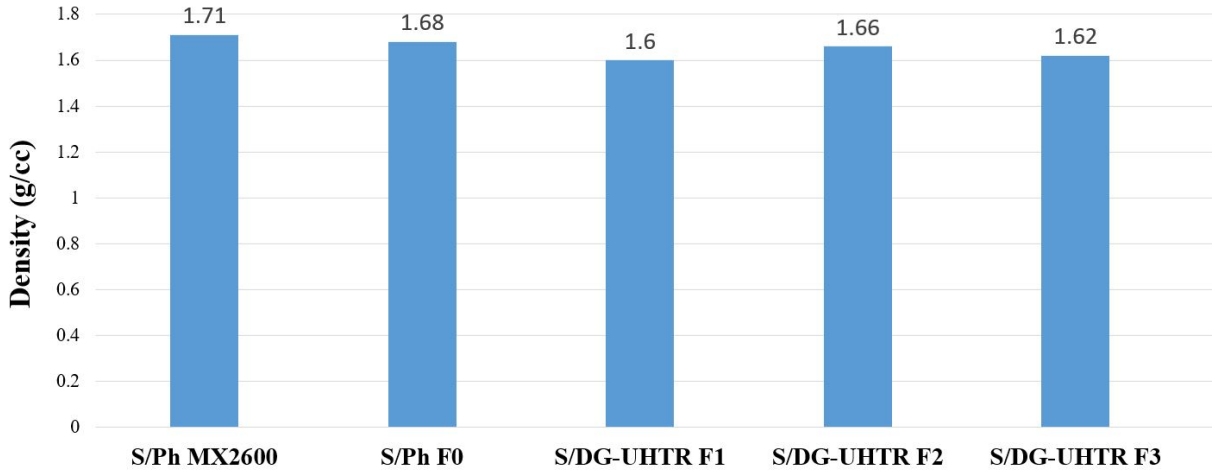


Figure 9. Density of various composites tested in this study.

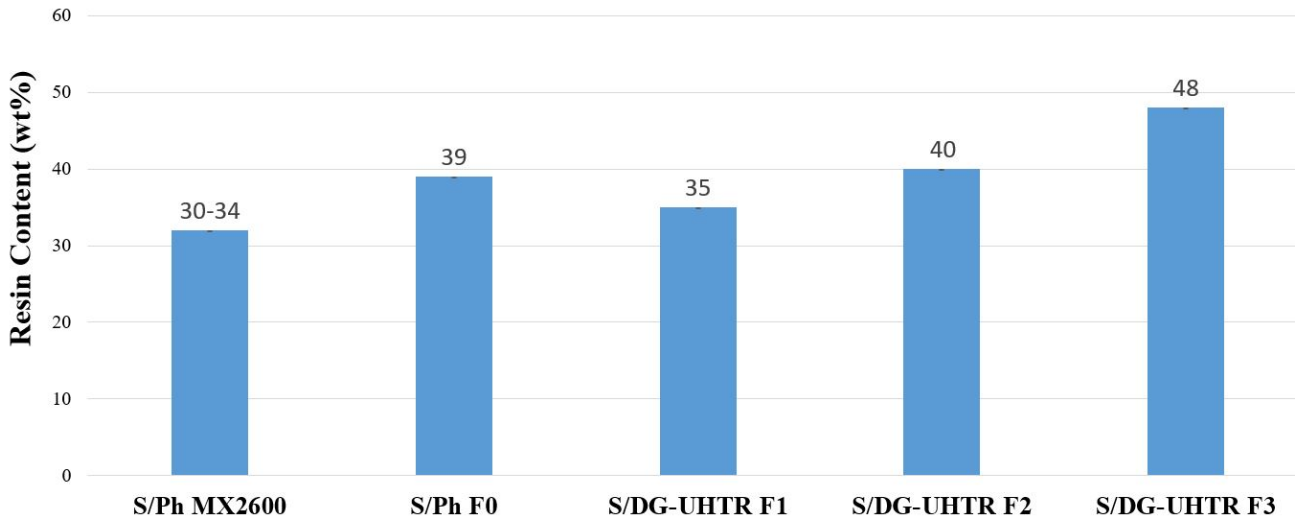


Figure 10. Resin content of the various composites tested in this study.

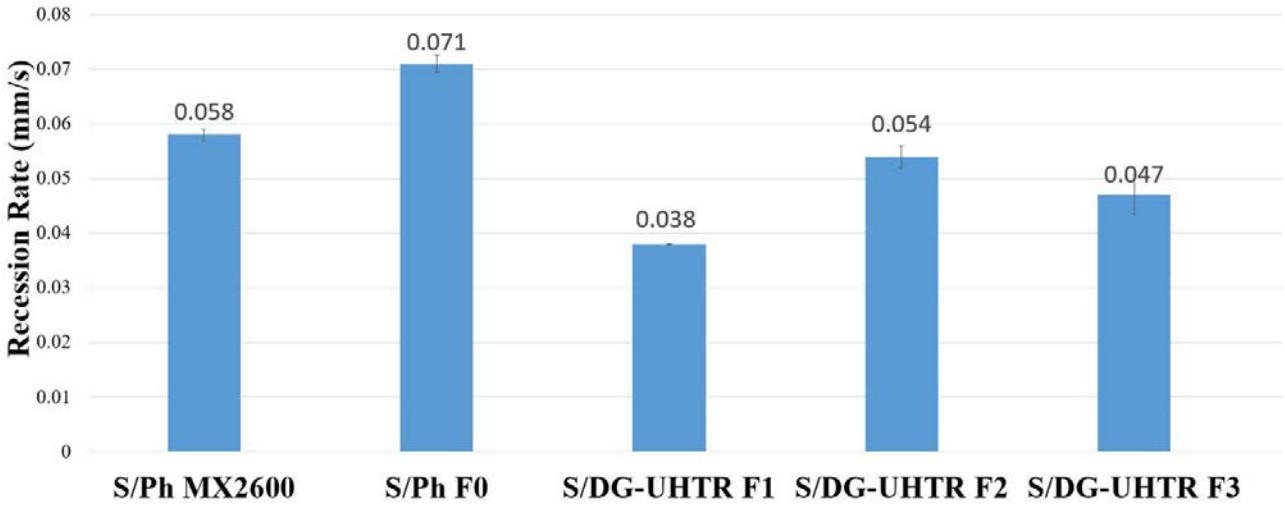


Figure 11. Recession rate of the various composites tested in this study.

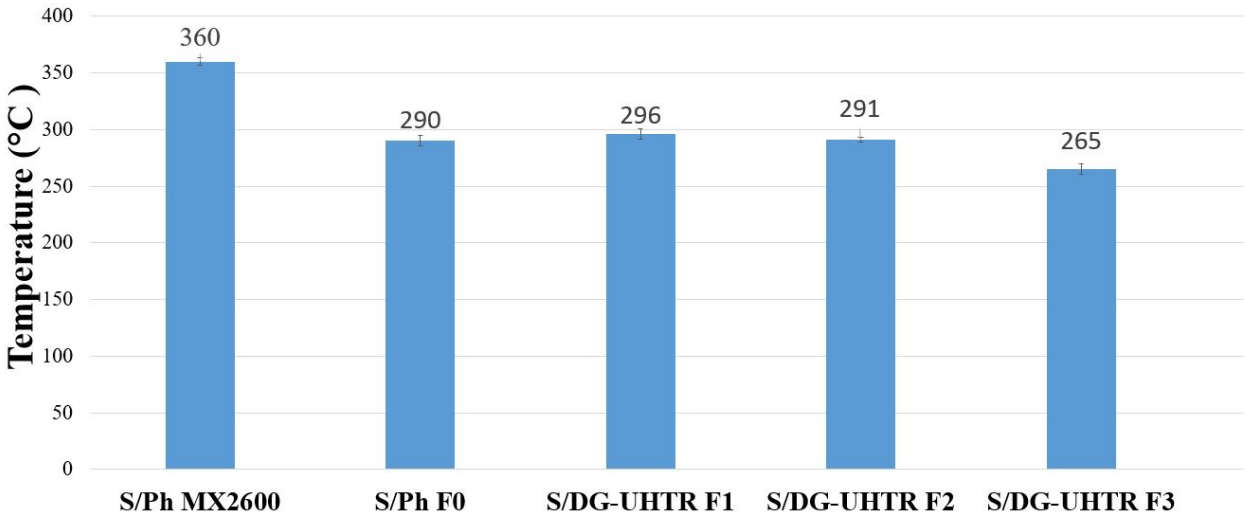


Figure 12. Peak heat soak temperature of the various composites tested in this study.

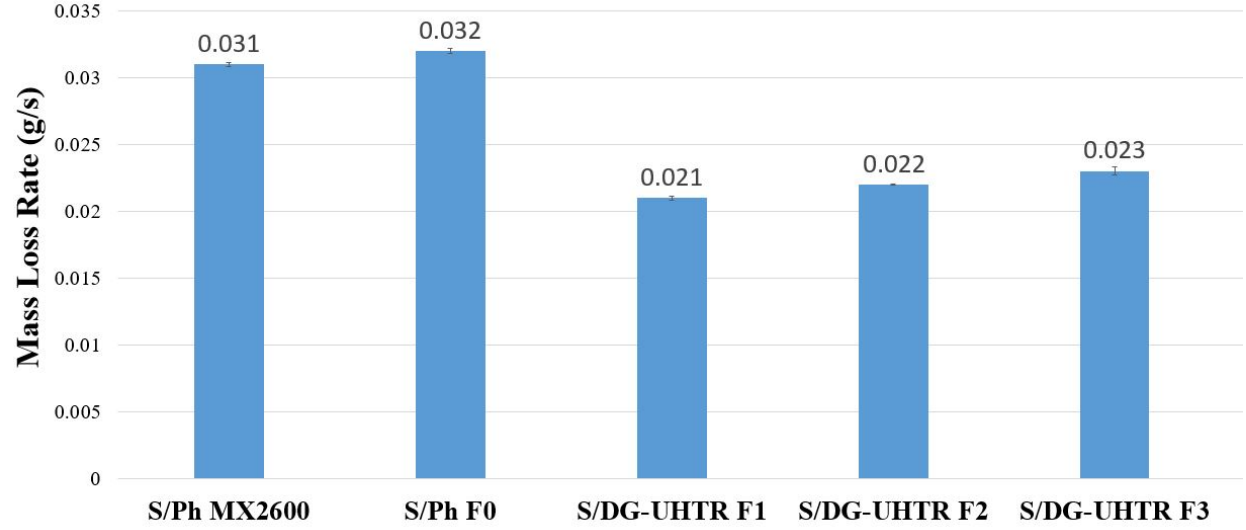


Figure 13. Mass loss rate of the various composites tested in this study.

Table 1. *Overview of collected OTB data*

	Density (g/cc)	Resin Content (wt%)	Recession Rate (mm/s)	Peak Heat Soak Temperature(°C)	Mass Loss (%)	Mass Loss Rate (g/s)
S/Ph MX2600	$1.71 \pm 1 \times 10^{-2}$	30-34	$0.058 \pm 2 \times 10^{-3}$	360 ± 18	$31.0 \pm 7 \times 10^{-1}$	$0.031 \pm 3 \times 10^{-4}$
S/Ph F0	$1.68 \pm 1 \times 10^{-2}$	39	$0.071 \pm 3 \times 10^{-3}$	290 ± 9	$29.0 \pm 5 \times 10^{-1}$	$0.032 \pm 4 \times 10^{-4}$
S/DG-UHTR F1	$1.60 \pm 1 \times 10^{-2}$	35	$0.031 \pm 3 \times 10^{-3}$	296 ± 8	$16.7 \pm 4 \times 10^{-1}$	$0.021 \pm 4 \times 10^{-4}$
S/DG-UHTR F2	$1.66 \pm 1 \times 10^{-2}$	40	$0.054 \pm 4 \times 10^{-3}$	291 ± 4	$19.5 \pm 5 \times 10^{-1}$	$0.022 \pm 1 \times 10^{-4}$
S/DG-UHTR F3	$1.62 \pm 1 \times 10^{-2}$	48	$0.047 \pm 7 \times 10^{-3}$	265 ± 10	$19.3 \pm 6 \times 10^{-1}$	$0.023 \pm 6 \times 10^{-4}$

Figures 9-13 and Table 1 summarize the OTB ablation testing data obtained. Figures 9 and 10 show the density and resin content of each of the formulations. Density was measured using the water displacement method in accordance with ASTM D792-08. The measured density of the MX2600 sample agreed with the reported value in the technical datasheet (TDS) of 1.71 g/cc [8]. From the MX2600 TDS, it was reported that it had a resin content of 30-34wt% based on the resin burn off method [8]. The F0, which was made by our lab, had a measured density of 1.68 g/cc, and a resin content of 39wt%. The higher resin content and lack of silica filler can explain the lower density of the F0 sample. Resin content for the samples in our lab was made by keeping track of the amount of silica fabric used to make the samples, and subtracting it from the final composite mass. The F1, F2, and F3 samples were found to have the increasing resin contents of 35, 40, and 48wt%. It was hypothesized that the density would decrease with higher resin contents. But the F1 sample was measured to have the lowest density and the F2 had the highest. This may be due to some inconsistencies between samples due to varying void content, or an error in the measurement.

A comparison of the recession rate for each formulation is shown in Figure 11, which was measured using an indicator placed in the center of the sample to subtract the final post-test thickness from the initial pre-test thickness. The F0 was found to have the highest recession rate at 0.071 mm/s, with the MX2600 having a lower recession rate of 0.058 mm/s. The F1 sample, which had the highest fiber content of the S/DG-UHTR samples, showed the lowest recession rate of 0.031 mm/s. The F2 showed the highest recession rate of all the S/DG-UHTR formulations at 0.054 mm/s, however it was still lower than both S/PH formulations. The F3 sample showed greater error and more cracking in the char than was observed in the other S/DG-UHTR samples. The F1 sample char appeared the most robust.

Figure 12 showed the peak heat soak temperature measured from the imbedded thermocouples. MX2600 showed the highest PHST of 360°C ± 18 and the highest error among the samples. There was a wider range of measured temperatures than seen in the other samples. It's possible this was due to flame wrap during testing. While the F0 showed a lower PHST, it also had a higher recession rate and a higher resin content. The F3 formulation, containing the most resin, showed the PHST of 265°C ± 10. The F1 formulation showed the highest PHST of the S/DG-UHTR formulations, but the lowest recession rate of all the samples. The S/DG-UHTR samples showed that as resin content was increased, lower PHST values were measured. The S/Ph samples showed the similar trend, but the MX2600 also contains silica filler in addition to lower resin content.

The mass loss rate for each sample during the 40s test was compared in Figure 13. The 35wt% DG-UHTR F1 showed the lowest mass loss rate of all the formulations at 0.021 g/s ± $4x10^{-4}$. As the resin content in the samples was increased, the mass loss rate also increased for the F2 and F3 formulations. The 40wt% F0 samples showed the highest mass loss rate of 0.032 g/s ± $4x10^{-4}$, which was slightly higher than the 30-34wt% MX2600.

3.3 Microstructural Analysis

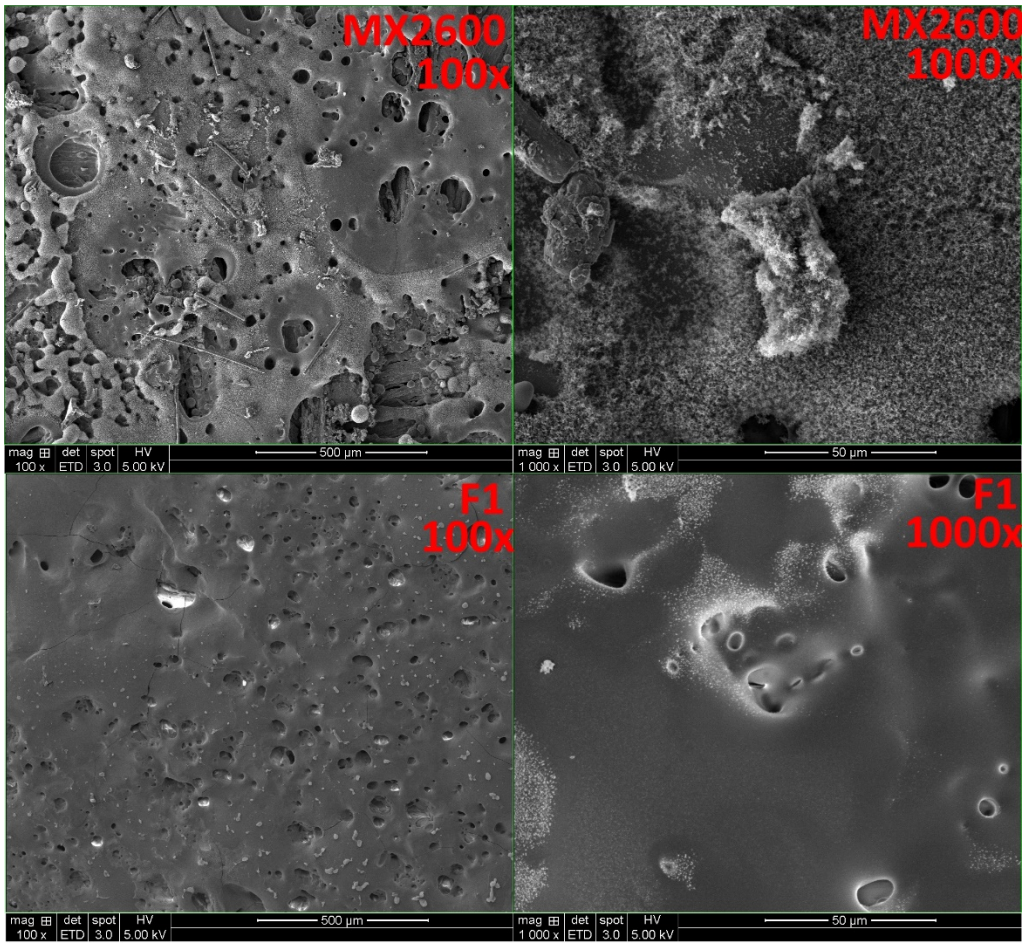


Figure 14. Top view SEM images of the char zone for MX2600 (top) and S/DG F1 (bot) in both 100x magnification (left) and 1000x magnification (right).

Post-test OTB samples were saved for microstructural analysis. A FEI Quanta 650 ESEM with Bruker EDX capabilities was utilized to examine the char layer. Low and high magnification images were taken of the MX2600 and F1 samples (Figure 14). At low magnification, there are a few differences that can be observed. They both show some dimpling across the surface, likely formed from the molten silica interacting with the pyrolysis gases. In the MX2600 sample, charred fiber, along with some of the porous char layer, covered moderately with molten silica, is observed, likely from the filler and fiber. The F1 does appear to have a more uniform surface, where you can't make out any fiber or porous char at low magnification.

At higher magnification, you can see the porous carbonaceous char across the MX2600 sample, whereas on the F1, it still appears smooth. EDX analysis confirms only the traces of Si, O_2, and C within the smooth charred surface. It's hypothesized that the preceramic resin, once exposed to the intense heat, chars and forms a ceramic shield. This ceramic shield helps prevent the entry of oxygen which will accelerate additional degradation.

4. SUMMARY AND CONCLUSIONS

4.1 Summary

The results of the S/Ph and S/DG-UHTR composites show the effect of each resin on degradation mechanism, thermal stability, flammability, and ablation properties. The char yield observed by TGA on the neat DG-UHTR resin was 86.5% and was found to range from 97.5% for F1 (35wt% resin) to 95.8% for F3 (48wt% resin) in the FRP samples. The F0 S/Ph (39wt% resin) was found to have lower thermal stability than the MX2600 S/Ph, which contained silica filler and a lower resin content of 30-34wt%. The dTGA peaks for all of the composite samples happened at lower temperatures than the neat resin samples. The MX2600 appeared to have different dTGA peaks than the neat SC-1008 sample tested, only showing two clear peaks instead of three. The F0 had a peak that also occurred at a much higher temperature than the MX2600, indicating lower temperature for mass loss to begin occurring. The dTGA peaks for the DG-UHTR composite formulations all occurred at temperatures around 600ºC, indicating higher thermal stability compared to the S/Ph composite samples.

Ablation data using the OTB revealed the MX2600 had better ablation performance than the F0 sample, in terms of recession rate and mass loss rate. However, F0 showed a lower average PHST of 290ºC compared to 360ºC for MX2600. The F3 formulation showed the lowest PHST value with 283ºC, but with an obvious outlier removed drops to 265ºC. The F1 formulation showed the lowest recession rate of 0.031 mm/s, which was 56.3% lower than the F0's 0.071 mm/s and a 46.5% lower than the MX2600's 0.058 mm/s. The F1 also showed the lowest mass loss rate and mass loss percent at 0.021 g/s and 16.7%, respectively. A microstructural analysis of the char morphology reveals the surface of the ablated S/DG composites has a very smooth appearance and might form a silicon oxide shield while ablating. Additional char morphology study of the cross-sections of the post-test samples is in progress.

The initial thermal and ablation properties exhibited by the S/DG-UHTR composites indicate this new ablative is a good candidate for TPS applications. Future work will focus on refining the process cycles to make TPS samples and characterizing mechanical properties such as tensile, compression, flexural, and shear strength for DG-UHTR FRP samples.

5. ACKNOWLEDGMENTS

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