

Experimental Characterization of Material Properties of Novel Silica/Polysiloxane Ablative

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DOI: 10.2514/1.A34044

This paper provides the details of the R&D of a new ablative material through a collaboration between The University of Texas at Austin and Techneglas LLC. The UHTR polysiloxane resin system is manufactured by Techneglas, based on a blend of polysiloxane chemistries. UHTR is used to fabricate silica fiber-reinforced composite materials by compression molding of prepreg. The objectives of this study are to process, fabricate, and experimentally characterize the physical, thermal, flammability, thermophysical, and ablation properties of the silica/UHTR composite. This silica/UHTR composite was compared with silica/phenolic fiber-reinforced polymers (FRPs) made in our lab as well as silica/phenolic (SC-1008) prepreg purchased commercially. The neat UHTR polysiloxane resin showed a higher char yield at 86.5% than the neat SC-1008 resin at 55.4%. Composites made from the UHTR resin showed exceptionally high char yields of 97.5, 96.7, and 95.8% for 35, 40, and 48 wt % samples, respectively. These composites showed superior recession rate, peak heat-soaked temperature, and mass loss rate during ablation testing using an oxy-acetylene test bed (OTB). Through-the-thickness thermal conductivity and specific heat capacity ranging from 50 to 600°C were measured using laser flash analysis and differential scanning calorimetry.

I. Introduction

H IGH-PERFORMANCE materials are urgently required for the ever-increasing demanding environments. Ablatives are used throughout aerospace and defense industries for a variety of applications, usually relating to the thermal protection of key structures. Polymeric ablatives offer key advantages over metals and ceramics, such as "low density, good thermal insulation capability, and good mechanical strength" [1]. Polymeric ablative is composed of resin, filler, and fiber reinforcement. Joint collaboration between The University of Texas at Austin and Techneglas, toward the R&D of a high-temperature fiber-reinforced composite, has shown great potential for use in polymeric ablative materials.

One of the most prevalent state-of-the-art (SOTA) resins used for such applications is SC-1008 phenolic resin. Its relatively low cost and an extensive characterization data give it a reputation as a proven material to protect the often-expensive structures it is applied to. The phenolic resin does come with environmental drawbacks, such as the presence of formaldehyde and short shelf life. Besides phenolic, there are few other polymeric ablative resins currently used in applications. Another SOTA high-temperature resin, cyanate ester, is currently being used in compression pads on the Orion space vehicle, whereas a majority of the thermal protection system (TPS) uses the same ablative used on the Apollo command module, AVCOAT 5026-39, which consists of epoxy-phenolic resin [2,3].

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Experimental data from the Koo Research Group (KRG) have identified several advantages of a new polysiloxane-based resin system, UHTR, which shows exceptional char yield, thermal stability, and flammability properties [4]. As a complete characterization of this resin's potential for use in ablatives is warranted, fiber-reinforced polymers (FRPs) were created using aerospace grade silica fabric and UHTR resin in this study. Silica/phenolic (S/Ph) ablatives manufactured in the KRG lab as a control and a commercially available S/Ph composite (MX-2600) from Cytec Solvay Group were used to compare with the silica/UHTR composites.

II. Background

A. Ablation Mechanism

Figure 1 shows the general mechanism of a charring polymer ablative. The ablative material is typically bonded to metal or composite structures with high-temperature adhesives that need to be protected from high heat and oxidation. For an ablative material to be used successfully, design engineers need to choose the appropriate material and thickness that can withstand a specific hostile environment. Two important features to evaluate the performance of an effective ablative are high ablation resistance and good insulative property.

In general, ablatives dissipate heat through thermochemical degradation involving endothermic reactions. However, there are additional mechanisms ablative employs that slow heat transfer and polymer decomposition. The formation of the char barrier on the surface of the material provides multifunction roles. Besides slowing the release of pyrolysis gases, which can have a cooling effect within the material, it also prevents direct flame contact with the remaining virgin material and helps block out oxygen attack. Because of the important role that char plays, it was hypothesized that the high char yield of the UHTR resin would enhance the protective mechanism, making it a desirable ablative material. There are also additional mechanisms that can help prevent the movement of oxygen through the char layer, such as ceramic shields that can form within the char matrix as decomposition occurs [5].

B. Resin Systems

SC-1008 is MIL-standard phenolic resole resin manufactured by Hexion. It is the most commonly used resin for manufacturing

Presented as Paper 2017-1367 at the 58th AIAA/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference, Grapevine, TX, 9–13 January 2017; received 28 July 2017; revision received 4 March 2018; accepted for publication 25 March 2018; published online 29 June 2018. Copyright © 2018 by J. H. Koo and K. Schellhase. Published by the American Institute of Aeronautics and Astronautics, Inc., with permission. All requests for copying and permission to reprint should be submitted to CCC at www.copyright.com; employ the ISSN 0022-4650 (print) or 1533-6794 (online) to initiate your request. See also AIAA Rights and Permissions www.aiaa.org/randp.

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Fig. 1 Diagram of the ablation process for a charring material [1].

ablative, such as carbon/phenolic (Cytec Solvay MX4926N [6] used for solid rocket motor nozzle), silica/phenolic (Cytec Solvay MX-2600 [7] used for solid and liquid rocket motor nozzles), and in the low-density ablator (FMI PICA [8] used for reentry vehicles). This phenolic resole resin has a char yield of 56%.

UHTR resin 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. Techneglas, LLC, is the sole manufacturer and has recently introduced a series of ceramic matrices specifically designed as binders for composite materials as flame shielding barriers [9]. This resin system offers the uniqueness of low-temperature curing that exhibits an extreme resistance to a high-temperature environment. It also possesses properties, such as low heat transfer, excellent chemical resistance, and low to no smoke or toxic fumes when exposed to flame sources. These fire, smoke, and toxicity (FST) characteristics are very desirable for fire-resistant polymers. The UHTR resin system in this study was found to have a char yield of 87% [4].

III. Experimental Approach

A. Composite Processing

To compare the ablation and thermal performance of each resin system, we incorporated each resin system into silica fiber and produce FRPs. Test samples were produced by infiltrating silica fabric with the resin systems to create prepreg, which was subsequently compression molded into FRPs. Additionally, a commercially made S/Ph, MX-2600 (Cytec Solvay) was obtained for comparison. This ablative uses a MIL-R-9299, Type II phenolic resin (30–35 wt %), silica fabric (64 wt %), and silica powder (4.5 wt %) [7].

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% SiO₂ silica fabric purchased from Cytec Solvay, which had a nominal weight of 19 oz/yd². 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 (RT) to 80°C, and held for 1 h. Then it was slowly heated to 90°C where it was held for 3 h, and subsequently heated to 95°C and held for 3 h. The resulting prepreg was then cut into 1.27 cm × 1.27 cm (1/2'' × 1/2'') 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 1000 psi for 5 min, 4000 psi for 10 min, and 8500 psi for 150 min. The sample was then allowed to cool to RT under pressure. F0 was produced at 39 wt % resin.

The UHTR resin was provided by Techneglas, LLC, and consisted of 35 wt % 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 layup and vacuum impregnated into aerospace grade silica fabric. The prepreg was made by curing the impregnated fiber at 80° C for 5 h under a 5 psi vacuum, and subsequently heating at 120° C for 5 h, with all heating rates at 1° C/min. Once chopped into the same-sized squares as the S/Ph, the S/UHTR prepreg was compression molded at 2000 psi for 120 min at 265°C. 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 were produced, containing varying resin contest of 35, 40, and 48 wt % resin, designated as F1, F2, and F3, respectively, in this study.

B. Flammability and Thermal Stability Properties Testing

ATA Instruments Hi-Res TGA 2950 Thermogravimetric Analyzer (TGA) was used to examine the thermal stability the char yield of the cured resin samples. A procedure for testing samples using TGA, developed by NASA, was adopted to better compare the various materials [10]. Each sample consisted of a 20 mg piece, which was dried at 150°C for 30 min. Then the sample was held at a constant heating rate of 20°C/min until it reached 1000°C. To prevent oxidative degradation, all heating was performed in a nitrogen atmosphere. This definition to determine char yield was repeated throughout TGA testing for new data presented later in this research.

Flammability properties were obtained using a Govmark microscale combustion calorimeter (MCC) 2 in accordance with ASTM D7309-2007. Each of the three resins was tested three times using the MCC. The pyrolyzer was heated from 100 to 750° C at a rate of 1°C/s.

C. Ablation Properties Testing

To evaluate the ablation performance of the samples, an oxyacetylene test bed (OTB) was used to simulate high heat flux conditions experienced by ablatives [11]. Several ablation properties can be measured during this test, including recession rate, mass loss, heat-soaked temperature, and surface temperature. We can also observe physical changes of the test sample during testing by using high-definition and infrared video cameras. A neutral 1.1:1 oxygento-fuel ratio was supplied to a #4 victor welding tip. A Vatell Gardon heat flux transducer (Thermogage 1000-54) [12] 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 1000 W/cm² for 40 s at a neutral oxy-acetylene flame.

Six 15.5-mm-diam cylindrical samples for each different material were machined via waterjet from the compression-molded samples. The thickness of the industry-made MX-2600 material was 12 mm and the thickness of the F0-F3 materials ranged from 14 to 16 mm. A miniature 0.55-mm-diam 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. Figure 2a shows a variety of equipment that monitored the surface of the sample during testing, including 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 ablative sample. Figure 2b shows the appearance of a test sample during OTB ablation testing. Figure 2c shows an S/UHTR F1 sample pretest (bottom left), F1 posttest (top left), a S/Ph MX-2600 sample pretest (bottom right), and MX-2600 posttest (top right).

An FEI Quanta 650 SEM was used to examine the microstructure of the posttest OTB samples. This SEM also uses a Bruker EDX system for elemental analysis. Top-view images of the charred samples were examined, as well as cross-sectional view images. To obtain the cross-sectional images, samples were encased in epoxy resin and cut in half.

IV. Results and Discussion

A. Flammability and Thermal Stability Results

As seen in Figs. 3 and 4, the MCC heat release curves show that the UHTR polysiloxane had one distinct heat release peak at about 630°C. The SC1008 had three heat release peaks at 335, 523, and 557°C, respectively. Heat release capacity (HRC) is an intrinsic

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Fig. 2 a) UT oxy-acetylene test bed (OTB) with advanced diagnostics experimental setup. b) Appearance of a sample during the testing. c) An S/UHTR F1 sample pretest (bottom left) and posttest (top left), and an S/Ph MX-2600 sample pretest (bottom right) and posttest (top right).



Fig. 3 Heat release curves for the two high-temperature resin systems.



Fig. 4 Heat release capacities for the two high-temperature resin systems.

materials property independent of material size and heating rate [13]. HRC values reflect materials' maximum heat release potential in complete combustion [14]. Among the two materials, the UHTR polysiloxane had the lowest HRC value of 36 J/($g \cdot K$). The HRC of SC-1008 phenolic was 53.3 J/($g \cdot K$). In summary, MCC results



showed that the UHTR material has high heat release temperature as well as low HRC values, indicating its good thermal stability and low flammability.

As seen in Fig. 5 and Table 1, the UHTR resin showed a high char yield of 86.5%. This was observed significantly higher than the 55.4% of the SC-1008 phenolic. Figure 6 shows the derivative of TGA curve in Fig. 5, which can be used to show at what temperature regions chemical degradation reactions are occurring. SC-1008 phenolic showed three distinct chemical reactions at 410, 511, and 655°C. The UHTR resin showed one distinct peak at 722°C and another minor peak at 873°C. The data indicate that the UHTR resin has the highest decomposition temperature (722°C) as compared with SC-1008 (410°C).

Each FRP formulation was evaluated for thermal stability using the same char yield definition. As seen in Fig. 7, the char yield for all materials increased significantly with the inclusion of silica fiber. The F1 formulation, containing 35 wt % 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 because the silica fiber can withstand temperatures much higher than 1000°C. An interesting phenomenon observed is that after 850°C, it appears that the S/UHTR formulations begin to slightly increase in mass. This may be due to unbalancing of the TGA instrument (an instrument error).

The 40 wt % phenolic resin sample, F0, showed the lowest char yield, with 85.3% of the mass remaining. The commercially bought MX-2600 showed a slightly higher char yield of 86.6%. This can be attributed to the fact that the MX-2600 contained an estimated

Table 1 Summary of collected TGA data

	Weight at 1000°C, %				10% Mass loss temperature, °C			
	5°C/min	10°C/ min	20°C/min	40°C/min	5°C/min	10°C/ min	20°C/min	40°C/min
SC-1008	61.4%	57.5%	56.2	57%	416	439	473	557
UHTR	85.9%	85.9%	86.5	90.2%	690	704	765	990

30-35 wt % 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 200 to 550°C range. It appears that the MX-2600 has better thermal stability between these temperatures and does not contain the sharper drop in mass observed at 250 and 400°C.

Figure 8 shows the derivative of the TGA curves for the five FRPs that helps to highlight some of the differences in the composites at the state of thermal degradation. The F0 sample showed three distinct peaks at 262, 430, and 580°C. These three peaks tended to happen at lower temperatures compared with the neat SC-1008 resin, which showed the three degradation reactions are occurring at 410, 511, and 655°C in Fig. 6. Interestingly, the first two degradation reactions of the F0 appear to happen before the first peak shown for the MX-2600, which occurred at 300°C. The second peak for the MX-2600 appears to blend in with the third peak, which happens at 544°C. This may be due to the silica filler, which is less likely to degrade before the phenolic resin and is helping the FRP to retain more of its mass during the degradation process occurring at these temperatures. The third F0







peak, occurring at 580°C, is 36°C higher than the third peak in the MX-2600.

The dTGA graphs for the S/UHTR composites show a similar trend seen in the phenolic samples, where the degradation peaks of the neat resin, illustrated in Fig. 6, happen at much lower temperatures. Whereas the peaks in the neat resin were not observed until around 722 and 873°C, the UHTR FRP's peak was observed around 600 and 780°C. The F2 formulation shows a slightly earlier first degradation reaction at around 587°C, compared with the 600°C seen for F1 and F3. All three formulations show a second minor peak occurring around 780°C.

B. Ablation Testing Results

Figure 9 shows a representative temperature versus time curve measured by the type-K thermocouple. The change in temperature of F0 increases more slowly than the MX-2600 samples but slower compared with the S/UHTR formulations. There was very little difference between the S/UHTR formulations in terms of peak heatsoaked temperature (PHST).





Average temperature vs time curve for the five ablatives. Fig. 9

Table 2 Summary of collected OTB data

Material	Density, g/cc	Resin content, wt %	PHST, °C	Recession rate, mm/s	Mass loss, %	Mass loss rate, g/s
S/Ph MX-2600	$1.71 \pm 1 \times 10^{-2}$	30-35	360 ± 18	$0.058 \pm 2 \times 10^{-3}$	$31.0\pm7\times10^{-1}$	$0.031 \pm 3 \times 10^{-4}$
S/Ph F0	$1.68 \pm 1 \times 10^{-2}$	39	290 ± 9	$0.071 \pm 3 \times 10^{-3}$	$29.0 \pm 5 \times 10^{-1}$	$0.032 \pm 4 \times 10^{-4}$
S/UHTR F1	$1.60 \pm 1 \times 10^{-2}$	35	296 ± 8	$0.031 \pm 3 \times 10^{-3}$	$16.7 \pm 4 \times 10^{-1}$	$0.021 \pm 4 \times 10^{-4}$
S/UHTR F2	$1.66 \pm 1 \times 10^{-2}$	40	291 ± 4	$0.054 \pm 4 \times 10^{-3}$	$19.5 \pm 5 \times 10^{-1}$	$0.022 \pm 1 \times 10^{-4}$
S/UHTR F3	$1.62 \pm 1 \times 10^{-2}$	48	283 ± 21	$0.047 \pm 7 \times 10^{-3}$	$19.3 \pm 6 \times 10^{-1}$	$0.023 \pm 6 \times 10^{-4}$

The MX-2600 S/Ph sample was found to have an average PHST of $360^{\circ} \pm 18^{\circ}$ C, and it also had the most variation between each of the temperature values for time curves (Table 2). The F0 S/PH sample was observed to have a lower PHST, with $290 \pm 9^{\circ}$ C. This may be because either F0 had a higher resin content or did not contain the silica filler. F1 and F2 were seen to have similar PHST values of $290 \pm 9^{\circ}$ C and $291 \pm 4^{\circ}$ C. The F3 S/UHTR formulation had the lowest PHST with an average of $265 \pm 10^{\circ}$ C from five samples, as an outlier was removed. The UHTR FRP data show a trend that higher resin content leads to a lower PHST.

The two-color IR pyrometer measured the surface temperature of a small point on the surface of the test sample. Figure 10 shows the 1800–2200°C region, where it was observed that overall, each sample had very similar surface temperatures of around 2050°C. The F0 and MX-2600 S/Ph samples both appeared to have most consistent surface temperatures, while the S/UHTR formulations showed greater variability with more peaks and valleys in the curves.

Figures 11–15 and Table 2 summarize the OTB ablation testing data obtained. Figures 11 and 12 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 MX-2600 sample agreed with the reported value in the technical datasheet (TDS) of 1.71 g/cc [8]. From the MX-2600 TDS, it was reported that it had a resin content of 30-34 wt % based on the resin burn off method [8]. The F0, which was made by the KRG lab, had a measured density of 1.68 g/cc, and a resin content of 39 wt %. The higher resin content and lack of silica filler can explain the lower density of the F0 sample. Resin content for the samples in the KRG 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 48 wt %. 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 caused by varying void content, or an error in the measurement.

A comparison of the recession rate for each formulation is shown in Fig. 13, which was measured using an indicator placed in the center





of the sample to subtract the final posttest thickness from the initial pretest thickness. The F0 sample was found to have the highest recession rate at 0.071 mm/s, with MX-2600 having a lower recession rate of 0.058 mm/s. The F1 sample, which had the highest fiber content of the S/UHTR samples, showed the lowest recession rate of 0.031 mm/s. The F2 sample showed the highest recession rate of all the S/UHTR formulations at 0.054 mm/s; however, it was still lower than both S/PH formulations. The F3 sample showed greater





Fig. 12 Resin content of the five composites tested in this study.



Fig. 13 Recession rate of the five composites tested in this study.



Fig. 14 Peak heat-soaked temperature of the five composites tested in this study.



Fig. 15 Mass loss rate of the five composites tested in this study.

error and more cracking in the char than was observed in the other S/UHTR samples. The F1 sample char appeared the most robust.

Figure 14 shows the PHST measured with the imbedded thermocouples. MX-2600 showed the highest PHST of $360 \pm 18^{\circ}$ C and the highest error among the samples. There was a wider range of measured temperatures than observed in the other samples. It is possibly due to flame wrapping during ablation testing. While 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 $265 \pm 10^{\circ}$ C. The F1 formulation showed the highest PHST of the S/UHTR formulations, but the lowest recession rate of all the samples. The S/UHTR samples showed lower PHST values as resin contents were increased. The S/Ph samples showed the similar trend, but the MX-2600 also contains silica filler in addition to lower resin content.

The mass loss rate for each sample during the 40 s test was compared in Fig. 15. The 35 wt % S/UHTR F1 showed the lowest mass loss rate of all the formulations at 0.021 g/s $\pm 4 \times 10^{-4}$. As the resin content in the samples was increased, the mass loss rate also increased for the F2 and F3 formulations. The 40 wt % F0 samples showed the highest mass loss rate of 0.032 g/s $\pm 4 \times 10^{-4}$, which was slightly higher than the 30–34 wt % MX-2600.

C. IR Surface Temperature and HD Surface Behavior Analysis

Figure 16 shows the HD camera still images collected concurrently with the IR images shown in Fig. 17. The three S/UHTR samples behaved differently from the MX samples. The S/UHTR samples appeared to flow as it ablated from liquid-like materials on the surface toward the outer edges, presumably the additional molten silica provided by the degrading S/UTHR composites. It was easier to make out the texture of silica fabric in the S/UHTR samples as the resin degraded. The 35 wt % resin F1 samples showed a slight difference in the last portion of the test, as its surface appeared to be more uniform and smooth than the F2 and F3 samples. The F2 and F3 samples had few differences, with the F3 showing a slightly more uneven surface during testing. As seen in the IR camera footage, this results in jagged surfaces, which results in regions of slighter cooler temperatures, as seen in the darker regions of the samples. This movement of surface material also accounts for the variability in the IR pyrometer surface temperature measurements, as the IR pyrometer can only focus on one point of the changing surface. Comparatively, the MX-2600 samples had a more evenly distributed surface texture. The footage showed some spherical aggregates on the MX-2600 samples as well, likely the melted silica fabric and filler, moving around on the surface. It was also observed that the F0 sample showed a brighter surface compared with the MX-2600 sample. It appears that the bright light mimics the shape of the chopped silica fabric, indicating that it is absorbing a large amount of thermal energy. The brighter regions on the 10 s mark of the MX-2600 and F0 were also observed in the IR camera footage to be hotter regions, which were not observed with the S/UHTR samples.

Using the IR camera, heat maps of the five samples were recorded. The heat maps are a useful tool in displaying a broad visual representation of the surface temperature data along the whole front face of each sample, because the IR pyrometer can only focus on a single point. Figure 17 displays heat maps from the four tested materials at different periods during the 40 s test. All samples displayed a relatively uniform temperature distribution along its face. When comparing the heat maps of S/DG samples with their respective palette bars, the data suggest that there are regions of hotter and cooler areas. Comparatively, the S/Ph samples had a very uniform temperature distribution across the sample. Unlike the S/UHTR composites, the MX-2600 sample displayed on the 10 s image still from the MX-2600 test has an orange hot spot on the left side of its front surface, indicating a hotter region. This hotter region during the first 10 s of the test was constantly seen in all MX-2600 samples. The F0 sample showed higher temperatures across the surface than the other samples during the early stages of the test.



Fig. 16 Compilation of HD video stills during testing for each material at 10, 20, 30, and 40 s.

However, the IR pyrometer does not reflect this, showing that it had the relative same surface temperature as the other tests. This may be because the IR pyrometer only measures one point rather than a holistic view of the sample. At the 40 s mark, the surface temperature appears to be much cooler, likely due to the buildup of char and because less virgin material is available for oxidation. The S/UHTR shows higher variability in the surface temperature later in the test than the MX-2600 does, resulting in the higher variability in surface temperature seen using the IR pyrometer focusing on one spot. S/UHTR IR versus time data appeared relatively similar for the three samples tested. The IR video of the F1 sample speared to show slightly higher surface temperatures during the last few seconds of the test, with some regions near the center approaching 2175°C. The IR pyrometer data do suggest that the S/UHTR samples consistently had higher surface temperatures than the other samples at the end of the test; however, the heat-soaked temperature is still low. With the lower resin content of F1, it may be forming a better ceramic shield, causing it to absorb more heat near the charred surface.

D. Microstructural Analysis

Charred samples from the OTB ablation testing were saved for posttest analysis. Top-view and cross-sectional SEM micrographs were taken of the 40 wt % resin samples, F0 and F2. These samples were chosen because they contain nearly equal resin and fiber content.

SEM micrographs in Figs. 18 (S/Ph F0) and 19 (S/UHTR F2) show different views of the posttest samples. The char images (Figs. 18a and 19a) show the top view looking at the char layer exposed directly to the flame. Both materials show a combination of smooth surface from the molten silica, and rough surface from the char. Dimpling in both materials can be observed, most likely caused by the pyrolysis gases being trapped in the molten silica layer as they move out of the material. The F0 sample (Fig. 18a) shows the presence of both charred resin and molten silica across the surface. More fibers are observed across the surface of the F0 char (Fig. 18a), whereas for the F2 char (Fig. 19a) no obvious fiber strands can be seen. The F2 char (Fig. 19a) appears to show a more uniform surface. The F2 char



Fig. 17 Compilation of IR video stills during testing for each material at 10, 20, 30, and 40 s.

appears to be smoother, with the resin that is exposed appearing to be more solid and in larger pieces than in the F0 char (Fig. 18a), which appears to be in smaller pieces. The size of the dimples appears to be relatively the same in both materials. The formation of some smaller silica spheres can be observed in both materials across the surface. In both materials, EDX analysis confirms that only the traces of Si, O₂, and C are detected within the smooth charred surface.

SEM micrographs of the side of the burned cylindrical sample were taken, focusing on the interface between the char and the virgin material, where the decomposition zone (Figs. 18b and 19b) and pyrolysis zone (Figs. 18c and 19c) would be located. The decomposition zone was defined as the area of heavy degradation, whereas the pyrolysis zone was defined as the area were the initial stages of decomposition were observed. The low-magnification images in Fig. 18 show that the propagation of the cracks in the F0 material is from pyrolysis to degradation zone. Higher magnification of the same area reveals changing of resin into char, as the outside of the fiber bundles begins to appear as part of a porous network. Low-magnification images of the pyrolysis and degradation zones of the F2 material (Fig. 19) reveal that during the initial stages of decomposition, there appears to be a heavy formation of spherical structures within the composite, and the fiber and the resin become hard to distinguish from the side of the sample. There is also the presence of some cracking in the F0



Fig. 18 SEM micrographs of S/Ph F0 of a) char zone (top view), b) decomposition zone (side view), c) pyrolysis zone (side view), and d) virgin zone (side view) at $100 \times (\text{left})$ and $1000 \times (\text{righ t})$ magnifications.

material (Fig. 18). The high-magnification micrographs of the same region show the spherical structures, showing a very homogenous surface, where it is difficult to distinguish fiber and resin. The decomposition zone shows a more solid looking char, and the fiber bundles can be more clearly made out. Compared with similar regions in the char of the F0 sample (Fig. 18a), the

char of the F2 sample (Fig. 19a) appears denser, as there is a noted absence of a porous char network. The virgin zone was defined as the area of material that had no signs of degradation. Micrographs of the virgin zone for both samples show good impregnation between the fiber bundles with the resin. No obvious difference was observed.



Fig. 19 SEM micrographs of S/UHTR F2 showing a) char zone (top view), b) decomposition zone (side view), c) pyrolysis zone (side view), and d) virgin zone (side view) at 100 × (left) and 1000 × (right) magnifications.

Figure 20 shows a cross-sectional view of the char in each sample, after they were encased in epoxy resin and cut in half using an end mill. Three SEM images were taken next to each other and combined into one overall image to provide a panoramic view of the char layer. Figure 20 shows the top-most section of the char layer, which was closest to the torch's flame. The F0 material (Fig. 20a) shows a

relatively rough-looking surface, consisting heavily of charred phenolic. Some delamination beginning to occur as well as the presence of some individual fibers are observed. The F2 material (Fig. 20b) appears to be more solid and smoother in texture. The shape of the fiber bundles can be observed, although they appear to be encased in either resin or molten silica. Both delamination and



Fig. 20 Cross-sectional-view SEM micrographs from char zone at the top of the sample for a) S/Ph F0 and b) S/UHTR F2 at 350× magnification.

formation of voids were observed near the upper part of the char. The middle section of Fig. 20 shows the char just below the top layer. It is easier to see the fibers present throughout the F0 sample (Fig. 20a) than in the F2 sample (Fig. 20b). This can be due to a much higher char yield of the F2 sample (Fig. 20b), and it is not losing as much resin as the F0 sample (Fig. 20a). Toward the bottom of Fig. 20, the F0 sample (Fig. 20a) shows charred resin around the exposed fiber bundles. The F2 sample (Fig. 20b) appears to show just the charred resin and no exposed fiber bundles were observed.

Because of the distinct difference observed between the SEM micrographs of the F1 (Fig. 20b) and F0 (Fig. 20a) samples, it is hypothesized that the UHTR resin, once exposed to the intense heat, chars and forms a ceramic shield consisting heavily of silica byproducts (Fig. 20b). This ceramic shield encases the fiber bundles and helps to retain more of the ablatives mass during thermal attack (Fig. 20b).

E. Thermophysical Properties

The ablative material's thermophysical properties, such as specific heat capacity and thermal conductivity, change under

external heat flux. Based on the results of the OTB ablation testing, the F1 sample was chosen for further thermophysical properties characterization of specific heat capacity (C_p) and thermal conductivity (k) in through-the-thickness (TTT) orientation in the virgin state. The purpose of this section is to provide the readers more material properties of the F1 sample. The C_p was measured using differential scanning calorimetry (DSC, Netzsch DSC-404 F1 Pegasus), and thermal diffusivity (α) was measured using laser flash instrument (LFA, Netzsch LFA457 Microflash). The amount of sample analyzed for the C_p measurements was 18.57 mg. The sample was placed in a standard alumina DSC pan/lid and the temperature-dependent DCS signal was obtained under a constant helium gas flow of 50 mL/min with identical heating and cooling rates of 5 K/min in the temperature range of 50-600°C. The temperature range was determined based on TGA and dTGA data, the first decomposition temperature of the ablative material.

For thermal diffusivity (α) measurements, a 10-mm-diam cylindrical sample with a thickness of 2.032 mm was spray-coated with a graphite layer. Thermal diffusivity was measured under a constant helium gas flow of 50 mL/min in the temperature range of





material.

50-600°C with 50°C steps. Thermal diffusivity values were measured by applying three laser shots for each temperature step. The results of TTT thermal diffusivity measurements of the virgin F1 material are shown in Fig. 21. In general, TTT thermal diffusivity value of F1 decreases as temperature rises from 50 to 600°C. These thermal diffusivity, density, and specific heat capacity values of the F1 material will be used to calculate the thermal conductivity values as a function of temperature of the F1 material.

The TTT specific heat capacity measurements for F1 are shown in Fig. 22. The oscillations below 60°C are due to the temperature stabilization and cannot be interpreted as a material C_p . It was observed that the C_p of the F1 material gradually rose from 1.04 to 1.21 J/(g \cdot K) as the temperature was increased from 50 to 150°C. There was also a gradual rise in C_p , 1.29–1.37 J/(g · K), between 250 and 300°C. The C_p remained relatively stable between 300 and 500°C. The oscillations above 550°C likely demonstrate that some changes are occurring in the sample properties, which matches up with the TGA and dTGA data for the F1 material, and a dTGA peak was observed at 600°C for F1, but there appears to be some slight mass loss before this peak.

Figure 23 shows the thermal conductivity data, which uses Eq. (1) and data from Figs. 21 and 22, and density (Table 2).



Fig. 23 Thermal conductivity measurements of S/UHTR F1 material.

$$k = \rho \cdot \alpha \cdot C_p \tag{1}$$

where k is thermal conductivity, ρ is the density, α is the thermal diffusivity, and C_p is the specific heat capacity. The measured density of F1 is 1.6 g/cm³ at RT (obtained from Table 2).

The virgin F1 material showed a thermal conductivity of 0.6 W/($m \cdot K$) from 60 to 100°C, but begins to slowly rise at 150°C until capping out around 0.68 W/($m \cdot K$) at 300. At 500°C, there is the beginning of rise in k. The oscillations in the C_p data, along with the TGA data, indicate degradation occurring around the 550-600°C range. The TTT thermal conductivity of F1 increases slightly from room temperature to 450°C. It increases significantly from 0.68 W/(m \cdot K) at 450°C to 0.85 W/(m \cdot K) at 550°C. There appears to be a change in thermal properties as the material begins to reach its degradation temperature, but it is unclear how the thermal conductivity of the F1 material in the char state behaves.

Table 3 shows the comparison of specific heat and thermal conductivity values of S/Ph (MX-2600) and F1 (S/UHTR) materials. The MX-2600 data were obtained from the technical data sheet of MX-2600 processed using curing cycle of 1000 psi at 149-163°C (300-325°F) for 30 min for 0.32 cm (1/8 in.) laminate [7]. The F1 data were obtained from this study. The specific heat of MX-2600 at 66°C is 1.13 J/($g \cdot K$), which is very similar to that of F1 [1.2 J/($g \cdot K$)]. The thermal conductivity values of MX-2600 at 149 and 260°C are 0.40 and 0.38 W/($m \cdot K$), which are lower than the thermal conductivity values of F1 at 149 and 260°C of 0.63 and 0.65 W/($m \cdot K$), respectively.

Table 3 Thermophysical properties of MX-2600 (S/Ph) and F1 (S/UHTR)

Material property	MX-2600 (S/Ph) ^a	F1 (S/UHTR) ^b
Specific heat at 66°C (150°F) Thermal conductivity at 149°C (300°F)	1.13 J/(g ⋅ K) 0.40 W/(m ⋅ K)	1.2 J/(g ⋅ K) 0.63 W/(m ⋅ K)
Thermal conductivity at 260°C (500°F)	0.38 W/(m \cdot K)	$0.65 \text{ W}/(\text{m} \cdot \text{K})$

^aProperties from MX-2600 technical data sheet [7] obtained when processed using cycle curing of 1000 psi at 149-163°C (300-325°F) for 30 min for 0.32 cm (1/8 in.) laminate. Specific heat was conducted at 66°C (150°F) per ASTM C-351. Thermal conductivity was conducted at 149°C (300°F) per ASTM C-177. ^bProperties from this study obtained when processed using cycle curing (see Sec. III.C) for 1.27 cm \times 1.27 cm (1/2 in. \times 1/2 in.) squares molding compound. Specific heat and thermal conductivity values were obtained during this study (see Sec. IV.E).

V. Conclusions

The processing, fabrication, and material properties of the S/UHTR composite were experimentally compared with the S/Ph composite. The results of the S/Ph and S/UHTR composites show the effect of each resin on thermal degradation mechanism, thermal stability, flammability, thermophysical, and ablation properties. The char yield observed by TGA on the neat UHTR resin was 86.5% and was also found to range from 97.5% for F1 (35 wt % resin) to 95.8% for F3 (48 wt % resin) in the composite samples. The F0 S/Ph (39 wt % resin) was found to have lower thermal stability than the MX-2600 S/Ph, which contained silica filler and a lower resin content of 30-35 wt %. The dTGA peaks for all of the composites happened at lower temperatures than the neat resin samples. The MX-2600 composite appeared to have different dTGA peaks from the neat SC-1008 resin tested, showing only two clear peaks instead of three. The F0 sample had a peak that also occurred at a much higher temperature than the MX-2600, indicating lower temperature for mass loss to begin occurring. The dTGA peaks for the S/UHTR composite formulations all occurred at temperature around 600°C, indicating better thermal stability compared with the S/Ph composite samples.

Ablation data using the oxy-acetylene test bed revealed that the MX-2600 had better ablation performance than the F0 sample, in terms of recession rate and mass loss rate. However, F0 showed a lower average peak heat-soaked temperature (PHST) of 290°C compared with 360°C for MX-2600. The F3 formulation showed the lowest PHST value of 265°C. The F3 formulation has better insulative properties than both the F0 and MX-2600 materials. 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 46.5% lower than the MX-2600'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. The microstructural analysis of the char morphology revealed that the surface of the ablated S/DG composites has a very smooth appearance and may form a silicon dioxide shield during ablation testing. SEM micrograph analysis showed the distinct difference between the char cross section, highlighting the formation of a ceramic shield of the S/UHTR composites during ablation process.

Thermophysical properties of through-the-thickness (TTT) specific heat capacity and thermal conductivity of F1 in the virgin state were characterized. DSC was used to determine the F1 material's TTT C_p values for temperatures ranging from 50 to 600°C, showing a low of 1.05 J/(g · K) and a high of 1.76 J/(g · K). MX-2600 has similar specific heat value of 1.13 J/(g · K) to F1's 1.2 J/(g · K) at 66° C. LFA and the measured density were used to determine the TTT thermal conductivity for the F1 material over the same temperature range. It was found that the material had a *k* value of 0.68 W/(m · K) at 50°C and a high value of 0.85 W/(m · K) at 600°C. Because the virgin F1 just begins to degrade around 600°C, it is unclear how the thermal conductivity values of 0.40 W/(m · K) (at 149°C) and 0.38 W/(m · K) (at 260°C) than F1 thermal conductivity values of 0.63 W/(m · K) (at 149°C) and 0.65 W/(m · K) (at 260°C).

The thermal and ablation properties of the S/UHTR composites indicate that this novel ablative is a good candidate for TPS application. Future work should be focused on optimizing the processing cycles to fabricate better test specimens and characterizing mechanical properties, such as tensile, compression, flexural, shear strengths and moduli, and adhesion for the S/UHTR composite. In-situ ablation recession and thermal sensing technology [15–17] should be applied to this novel S/UHTR composite to obtain in-situ ablation recession and thermal data [15–17] for material response modeling using the NASA CHAR code [18]. The Koo Research Group is currently developing a 3D material response model using the CHAR code with experimental data of PICA [15,16], AVCOAT [15,16], 2D carbon/phenolic [16], and 3D carbon/phenolic ablatives [19].

Acknowledgments

The authors greatly appreciate the financial support from Techneglas, LLC, for this research. The authors also thank UT Austin students contributed to this project. Several pieces of advanced diagnostics equipment (HD video and IR video cameras) from NASA Johnson Space Center were on loan to the Koo Research Group and were used in this study.

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