

PROCESSING AND CHARACTERIZATION OF BASALT FIBER REINFORCED CERAMIC COMPOSITES FOR HIGH TEMPERATURE APPLICATIONS USING POLYMER PRECURSORS

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ABSTRACT

The development of high temperature structural composite materials has been very limited due to the high cost of the materials and the processing needed. Ceramics can take much higher temperatures, but they are difficult to produce and form in bulk volumes. Polymer Derived Ceramics (PDCs) begin as a polymer matrix, allowing a shape to be formed and cured and then to be pyrolyzed in order to obtain a ceramic with the associated thermal and mechanical properties. The two PDCs used in this development are polysiloxane and polycarbosilane. Polysiloxanes contain a silicon oxycarbide backbone when pyrolyzed up to 1000°C. Polycarbosilane, an organosilicon polymer, contain a silicon-carbon backbone; around 1200°C, β -SiC begins to crystallize.

The use of basalt in structural and high temperature applications has been under development for over 50 years, yet there has been little published research on the incorporation of basalt fibers as a reinforcement in composites. Basalt is a naturally occurring material found in volcanic rock. Continuous basalt fiber reinforced PDCs have been fabricated and tested for the applicability of this composite system as a high temperature structural composite material. Thermal and mechanical testing includes oxyacetylene torch testing and three point bend testing.

1. INTRODUCTION

In the aerospace industry, as the need for high performance vehicles grows, the need for materials which can meet these high performance levels becomes even more important. Materials must withstand high loads and high temperatures while remaining lightweight. Fiber reinforced composites have become more prevalent as structural materials because of their strength to weight ratio. This would be ideal for a lightweight, high temperature application. The combination of fibers and matrix can be designed to specifically meet unique requirements. The development of high temperature structural composite materials has been very limited due to the high cost of the materials and the processing needed. Polymer matrix composites are popular for structural components because the resins used have low viscosity, allowing complex shapes to be formed prior to curing. But the maximum operating temperatures of typical polymers such as epoxies and bismaleimides are 170°C and 260°C, respectively. Ceramic matrix composites are able to handle higher temperatures, and the continuous fiber reinforcement provides increased strength in an otherwise brittle material.

1.1 Polymer Derived Ceramics

The main methods of producing a continuous fiber reinforced ceramic matrix composite are chemical vapor infiltration, reactive melt infiltration, slurry impregnation and hot pressing, and polymer infiltration and pyrolysis. This study uses polymer infiltration and pyrolysis (PIP) which starts off with a polymer precursor that is combined with the fibers and cured in an oxygen environment to allow for crosslinking, inhibiting any further shape changes. The part is then pyrolyzed at high temperatures in an inert environment, removing the polymer chains and leaving the ceramic backbone. The part then requires re-infiltration with the polymer and further pyrolysis cycles in order to increase the density of the ceramic matrix which maximizes the ceramic content and increases the strength. [1]

Several polymers have been studied for use as a polymer derived ceramic (PDC) for PIP processing. Polysiloxanes (PSX) contain a Si-O-C, or silicon oxycarbide, backbone when pyrolyzed up to 1000°C, and convert to SiC when pyrolyzed to temperatures above this. Polysiloxanes are relatively inexpensive in comparison to other PDCs, but it requires higher pyrolysis temperatures in order to obtain silicon carbide. [2]

Polycarbosilane, an organosilicon polymer, contains a silicon-carbon backbone. Work with polycarbosilanes began in the 1970s under Yajima, who developed silicon carbide continuous fibers. [3] Curing polycarbosilane turns the Si-H and Si-CH₃ bonds into Si-O-Si and Si-O-C due to oxidation. Alteration of the curing conditions, such as ramp rate, curing temperature, and dwell time, affect how much oxidation occurs. A study by Ly et. al. found that a slower ramp rate, less than 0.5°C/min, and longer curing time, around 1.5 hours at 200°C, allowed for more crosslinking. [4] During the pyrolysis, the resin forms a Si-O-C phase; around 1200°C, β-SiC begins to crystallize. This is similar to the pyrolysis of the polysiloxane, except that the transformation to β-SiC occurs at a lower temperature. A follow up study by Ly et. al. found that pyrolyzing uncured polycarbosilane resulted in β-SiC crystallization at even lower temperatures, around 1000°C. [5] Therefore, curing and pyrolyzation methods can be adjusted to get the optimal properties needed for the application.

Several studies have researched carbon fiber reinforced ceramic matrix composites, but only a few have looked at the PIP process using polycarbosilane reinforced with carbon fiber. For ceramic matrix composites, the flexural strength is increased when the fibers are weakly bonded to the matrix and instead absorb energy through the friction between the fiber and the matrix. When the bond is strong, the fibers have a brittle failure that occurs at the same loading as the matrix; this prevents the fibers from serving as a reinforcement. [6] Another study tested the flexural strength of carbon fiber reinforced PCS composites and found the strength to be 27 MPa and the failure to be less brittle than monolithic ceramics. [7]

1.2 Continuous Basalt Fiber

Basalt is a good candidate for fiber reinforcement due to its high elastic modulus, heat resistance, and acoustic dampening. [8] The literature gives tensile strength values from 1500 to 4000 MPa and operating temperatures around 800°C. Above this, degradation begins to occur. The melting point of basalt is around 1400°C. Basalt fibers have also been found to perform well after being immersed in various environments. [9] Basalt is a good alternative to glass and carbon as reinforcement. Carbon fibers are widely used because of their high thermal and mechanical properties, but they are expensive. Glass fibers are less expensive, but have lower thermal and mechanical properties than carbon fibers. Basalt fibers are around the same cost as

glass fibers, but they have mechanical and thermal properties closer to carbon fibers. This makes basalt an ideal choice for consideration.

The composition of the basalt is very important for both the fabrication and the resulting properties of basalt fibers. Although the exact composition varies depending on the geographical location and the rate of cooling as the molten lava reaches the surface, basalt is composed of three main components: plagioclase, pyroxene, and olivine. [8] Currently, the majority of the basalt used to fabricate continuous basalt fibers comes from the Ukraine and Georgia. Basalt from this region produces fibers with the qualities needed to make strong composites. [10]

One study looked at the use of basalt fiber composites for fire protection. This study cites the high temperature capabilities and relatively low cost of basalt fibers. A flame test was performed with an oxyacetylene torch. Two configurations were used: one with woven basalt in an epoxy matrix and one with chopped basalt in concrete. Both tests showed better results than the fiberglass and polyester resin composite panel. The low thermal conductivity keeps the high temperature from spreading quickly through the panel. [11]

Because of the high temperature stability of basalt fibers, a series of studies was performed on the mechanical behavior of the fibers alone as well as the effect of partial pyrolysis on a polysiloxane matrix reinforced with basalt fibers. The high temperature tensile properties of basalt fibers were found to be similar to that of glass fibers. Unidirectional basalt fiber reinforcement in a polysiloxane resin, which tested pyrolysis temperatures from 400°C to 800°C, found that the fiber is prone to elongation at temperatures above 600°C and that microcracking in the matrix causes cracking in the fiber as well; the authors suggest that further attention be paid to the processing pressure and temperature rates in order to minimize this affect. The results of the study found that the elastic and shear moduli of the composites increased with oxidative heat treatment, and the authors attribute this to further transformation of the polymer matrix to a ceramic matrix. [12]

Another study performed mechanical testing on unidirectional basalt fiber/polysiloxane composites, looking at both the pyrolysis temperature (650°C or 750°C) and the effect of fiber lubrication. This study found that the lubrication and the lower pyrolysis temperature increased the shear modulus but did not have significant effect on the elastic modulus, which is dominated by the fibers. [13] A more recent study tested plain weave basalt fiber/polysiloxane composites at pyrolysis temperatures up to 800°C. The flexural strength of the specimens pyrolyzed at 450°C only reaches 30 MPa. As the pyrolysis temperature increases to 650°C, the flexural strength increases to slightly above 100 MPa. Above 650°C, there is a slight decrease in the flexural strength; this variation in flexural strength is due to the amount of ceramic conversion that has occurred. [14]

2. EXPERIMENTATION

2.1 Panel Fabrication

A polysiloxane, SPR-688, and a polycarbosilane, SMP-10, both from Starfire Systems, are used for this study. Material properties are given in Table 1. The cure cycle for each of the PDCs was refined by curing resin only samples and then thin samples made with basalt fiber. The cure cycle used for the test panels is given in Table 2. Curing was performed in the autoclave under 28 inHg of vacuum. Small specimens with six layers of basalt biaxial fabric were fabricated using a wet layup process and cured. 2" x 3" specimens were cut from these panels in order to pyrolyze them in a tube furnace. The pyrolysis cycle in the tube furnace is given in Table 3. The

hold time at 850°C ranged from 60 minutes to 150 minutes in order to determine the length of time required to get the most mass loss, which correlates to the most ceramic conversion; it was determined that 90 minutes is the optimal hold time.

Table 1. Properties of PDC Resins

	SPR-688	SMP-10
Density (g/cm ³)	1.11	0.998
Viscosity (cPs at 25 degC)	300-2000	40 to 100
Flash Point (degC)	93	89

Table 2. Cure Cycles

	Polysiloxane	Polycarbosilane
Ramp Up	3°C/min	3°C/min
Hold Temp	100°C	170°C
Hold Time	90 min	90 min
Ramp Down	3°C/min	3°C/min

Larger test panels were then fabricated and pyrolyzed in a kiln. These larger panels require a slower cure process in order to allow the heat to evenly distribute throughout the part. 6" x 6" panels were made with polysiloxane and 12 layers of biaxial basalt fabric, resulting in 0.25" thick panels. The polysiloxane panels were able to be pyrolyzed with the cycle given in Table 3 with minimal shape change.

Table 3. Pyrolysis Cycle for Polysiloxane in Kiln

Ramp Up	1°C/min
Hold Temp	650°C
Ramp Up	2°C/min
Hold Temp	850°C
Hold Time	90 minutes
Ramp Down	5°C/min

The first panels made with polycarbosilane also used this cycle, but they were bowed in the middle after pyrolysis. In order to eliminate this, various cycles were attempted to slow down the heating and allow the part to heat more evenly. Table 4 shows the cycles used. Although the shape change was reduced with the slower cycles, there was still some curvature in the panels.

Table 4. Cure Cycles of Polycarbosilane Panels for Torch Testing

LBF203	LBF204	LBF206	LBF207	LBF208
1°C/min	1°C/min	1°C/min	1°C/min	1°C/min
650°C	200°C	200°C	260°C	650°C
No Hold	60 min	60 min	180 min	No Hold
2°C/min	1°C/min	1°C/min	1°C/min	2°C/min
850°C	400°C	300°C	300°C	850°C
90 min	60 min	60 min	60 min	90 min
-5°C/min	1°C/min	1°C/min	1°C/min	-1°C/min
	600°C	500°C	500°C	
	60 min	60 min	60 min	
	1°C/min	1°C/min	1°C/min	
	700°C	600°C	600°C	
	60 min	60 min	60 min	
	1°C/min	1°C/min	1°C/min	
	850°C	700°C	700°C	
	60 min	60 min	60 min	
	-0.75°C/min	1°C/min	1°C/min	
	350°C	850°C	850°C	
	-1°C/min	60 min	60 min	
	100°C	-0.75°C/min	-0.75°C/min	
		100°C	100°C	

Five 6" x 6" panels of each PDC were fabricated for the Oxyacetylene Torch Testing. Table 5 lists the panel IDs and their as fabricated data. After pyrolysis, the panels shrunk slightly to 5.5" x 5.5". For the polysiloxane panels, the average resin content is 21% and the average resin mass retained after pyrolysis is 71%. For the polycarbosilane panels, the average resin content is 20% and the average resin mass retained after pyrolysis is 84%. The first set of testing was performed on these panels, which did not undergo reinfiltration and further pyrolysis cycles. One panel was also made for bend testing. Table 6 shows the fabrication data for this panel.

Table 5. Fabrication Data

Panel ID	PDC Used	CURED PANEL		PYROLIZED PANELS	
		Fiber Volume Fraction	Resin Content by Weight	Mass Retained	Resin Retained
LBF103	SPR-688 (Polysiloxane)	56.15%	23.45%	94.66%	76.27%
LBF104		52.55%	19.49%	93.20%	69.28%
LBF105		52.11%	21.37%	92.96%	70.54%
LBF106		52.00%	19.35%	93.12%	69.00%
LBF107		52.09%	20.01%	93.09%	69.61%
LBF203	SMP-10 (Polycarbositane)	54.72%	18.73%	95.51%	76.67%
LBF204		49.48%	19.39%	97.95%	89.41%
LBF206		49.45%	20.88%	97.10%	86.67%
LBF207		49.69%	21.01%	See Note 1	
LBF208		49.59%	19.73%	See Note 1	

Note 1: Post pyrolysis weight was not acquired prior to panel testing; therefore these values were not able to be calculated

Table 6. Panel Fabrication Data for Bend Test #1

Panel ID	PDC Used	Layup	POST CURE		POST PYROLYSIS	
			Fiber Volume Fraction	Resin Content by Weight	Mass Retained	Resin Retained
LBF214	SMP-10	[0/90/45/-45]3s	43.85%	18.82%	97.78%	88.19%

2.2 Reinfiltration

In order to decrease the voids in the ceramic matrix that occur during pyrolysis, panels are reinfiltrated with the PDC and then pyrolyzed again. Reinfiltration was performed in a vacuum chamber. The part was covered in resin and then put under vacuum for 90 minutes. The part was then pyrolyzed again. Panels were made using SMP-10 and a plain weave basalt fabric. In order to further reduce the warping in the panel after pyrolysis, the panel layup was changed. The layup for LBF224 and LBF225 resulted in flat panels. All the panels shown in Table 7 underwent the reinfiltration and pyrolysis cycle twice except for LBF217. A panel was also made for bend testing. Table 8 gives the fabrication and reinfiltration data for this panel.

Table 7. Fabrication Data for SMP-10 Panels with Plain Weave Basalt Fabric

Sample ID	POST CURE FRACTIONS		PYROLYSIS		REINFILTRATION #1		REINFILTRATION #2	
	Fiber Volume	Resin Content	Mass Retained	Resin Retained	Resin Retained	Resin Content	Resin Retained	Resin Content
LBF217	59.61%	16.24%	98.26%	89.26%	95.45%	16.66%	N/A	N/A
LBF222	55.87%	17.69%	94.89%	71.10%	76.21%	19.01%	79.29%	22.63%
LBF224	55.07%	18.54%	95.34%	94.50%	72.04%	19.26%	83.18%	22.64%
LBF225	54.09%	17.69%	95.28%	95.28%	67.40%	19.09%	77.26%	22.38%

Table 8. Panel Fabrication Data for Bend Test #2

Sample ID	PDC Used	Layup	POST CURE		PYROLYSIS	
			Fiber Volume Fraction	Resin Content by Weight	Mass Retained	Resin Retained
LBF215	SMP-10	[45/90/-45/0] _s	57.36%	15.10%	99.37%	96.38%
			REINFILTRATION #1		REINFILTRATION #2	
			Resin Retained	Resin Content by Weight	Resin Retained	Resin Content by Weight
			83.85%	19.29%	95.54%	20.12%

3. MATERIAL TESTING RESULTS

In order to characterize the material, Scanning Electron Microscopy/Energy Dispersive Spectroscopy was performed, as well as X-Ray Diffraction. Panels underwent thermal testing by performing oxyacetylene torch testing. Three point bending was also performed to assess the mechanical performance of the composite.

3.1 Material Characterization

Scanning electron microscopy (SEM) was performed using a Zeiss ULTRA 55 Field Emission Gun SEM at the Materials Characterization Facility. This machine also performs Electron Dispersive Spectroscopy (EDS) with a Noran System 7 EDS system with Silicon Drift Detector. Figure 1 shows SEM images of basalt fibers. The image on the left is fibers taken from the biaxial fabric and the one on the right is from the plain weave fabric. The fibers are very similar in size. Figure 2 shows the elemental composition of fibers from the plain weave basalt.

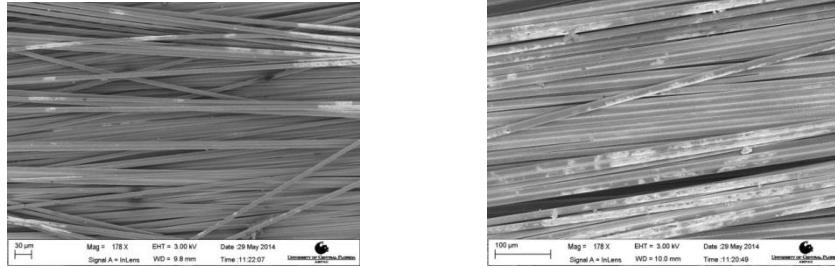


Figure 1. SEM of Basalt Fibers: Biaxial Basalt (Left), Plain Weave Basalt (Right)

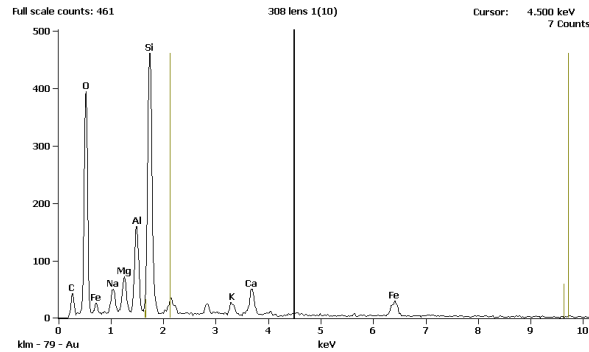


Figure 2. EDS of Plain Weave Basalt Fibers

Specimens were taken from the panels listed in Table 5 and Table 7. Figure 3 shows cross sections of a polysiloxane and a polycarbosilane panel which only received one pyrolysis cycle and no reinfiltration. The images show good penetration of the resin into the fiber tow, although the polycarbosilane panel has more voids in the matrix surrounding the fibers. Figure 4 shows EDS of the matrix. The gold is due to the gold sputtering applied to the sample for conductivity, and the calcium and aluminum are most likely due to the basalt fiber. The main elements are silicon, oxygen, and carbon, which are expected for the temperature at which these parts were pyrolyzed.

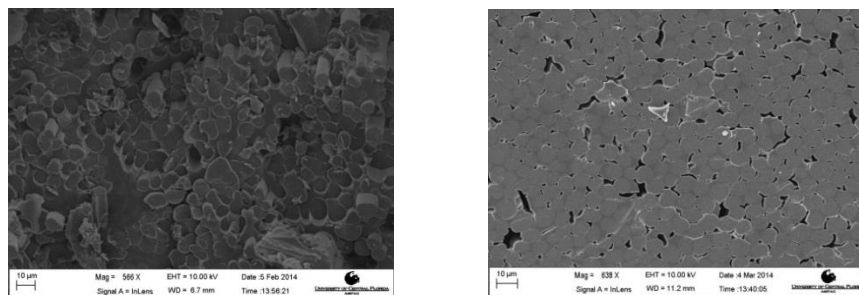


Figure 3. SEM Images, Left: Polysiloxane Panel (LBF105), Right: Polycarbosilane Panel (LBF208)

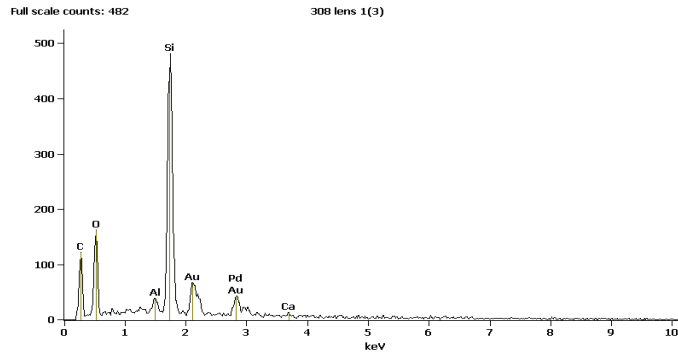


Figure 4. EDS of Matrix Material from Panel LBF105

Figure 5 and Figure 6 are SEM and EDS, respectively, from polycarbosilane panels which were pyrolyzed to 700 °C and had 2 reinfiltration cycles. The SEM image shows very few voids in the matrix surrounding the fibers. Because these panels are only pyrolyzed to 700 °C, the matrix contains silicon, carbon, and oxygen; the other elements present are due to the basalt fiber.

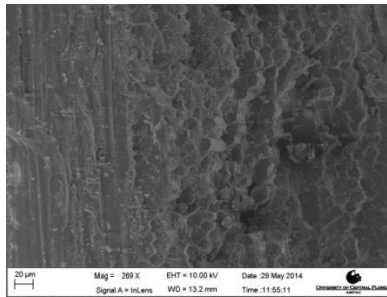


Figure 5. SEM Image of Polycarbosilane Panel (LBF225)

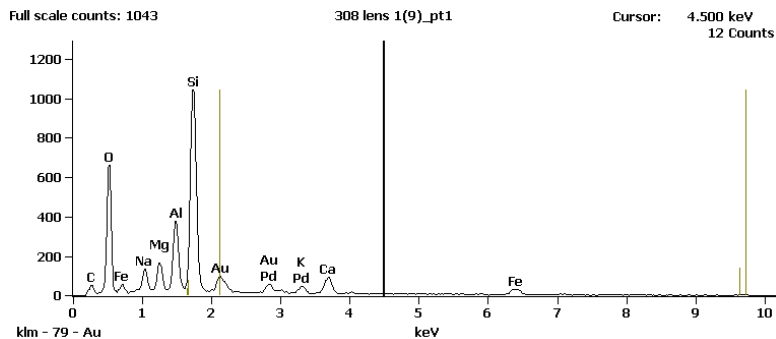


Figure 6. EDS from Polycarbosilane Panel (LBF225)

3.2 Flexural Testing

Two panels were fabricated and cut into specimens for bend testing, referencing ASTM C1341. This test is specifically for 3 and 4 point bending of continuous fiber reinforced ceramic composites. 3 point bending was performed on an Instron in the Mechanical Engineering Lab. The first panel tested only received one pyrolysis cycle and no reinfiltration (see Table 6). It was then cut into (8) 19 mm wide specimens. The specimens were 6 mm thick and they were tested at a span of 152 mm, which gives a thickness to span ratio of 24:1. The specimens were loaded at a rate of 0.041mm/min. Figure 7 shows the load vs. the displacement for all 8 specimens. There is

very little displacement before failure, which is common for ceramic materials. The fibers in the part allow for more flexure which increases the overall strength. Table 9 shows the flexural strength in each specimen; the average flexural strength was 33.5 MPa.

Table 9. Bending Test Panel #1 Results

TEST	MAX LOAD (N)	Strength (MPa)
1	113.88	33.98
2	85.59	25.54
3	148.60	44.34
4	109.52	32.68
5	126.12	37.63
6	104.33	31.13
7	106.34	31.73
8	95.49	28.49

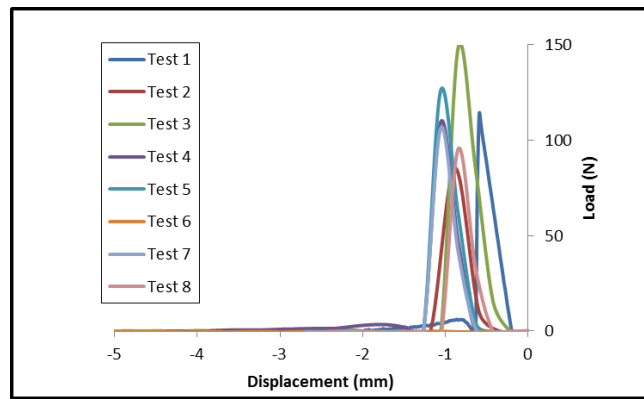


Figure 7. Displacement vs. Load for Test Panel #1

Test panel #2 received two reinfiltration cycles to increase the ceramic content (see Table 8). This panel was then cut into (5) 15 mm wide specimens for testing. The specimens were 4 mm thick and they were tested at a span of 128 mm, which gives a thickness to span ratio of 32:1. The specimens were tested at a rate of 0.0594 mm/min. Figure 8 shows the displacement vs. load for each specimen. Table 10 shows the flexural strength results with an average of 16.3 MPa.

Table 10. Bending Test Panel #2 Results

TEST	MAX LOAD (N)	Strength (MPa)
1	18.09	14.36
2	21.00	16.66
3	19.26	15.29
4	20.52	16.29
5	23.79	18.88

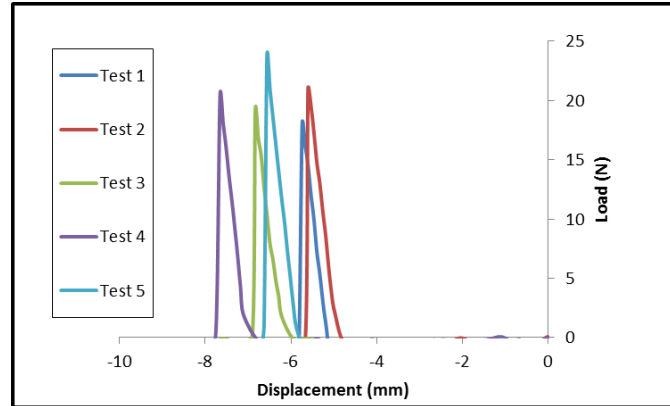


Figure 8. Displacement vs. Load for Test Panel #2

The reinfiltrated panels show about half of the flexural strength of the pyrolysis only panels. This could be because the span to thickness ratios were different, or because the crosshead speed was faster for the reinfiltrated panels. It could also be because a different fabric form was used, or the reinfiltration cycles strengthened the bond between the fibers and the matrix causing the fibers to fail in a brittle manner. Further testing and analysis would have to be done to determine the exact reason.

3.3 Oxyacetylene Torch Testing

Torch testing was performed, closely following the ASTM E285 Method, except there was no temperature reading for the front of the panel. The panels were trimmed to 4" x 4" panels, and a thermocouple was attached to the back. Testing set up is shown in Figure 9. The panel is held inside a metal frame which is bolted together, and a thermocouple is bonded to the center of the back of the panel. A metal cover is placed in front of the panel as the flame is ignited. After the flame is focused, the cover moves to the side and the panel slides forward on the rail, putting it 3/4" from the nozzle. The thermocouple data is recorded for the duration of the test.

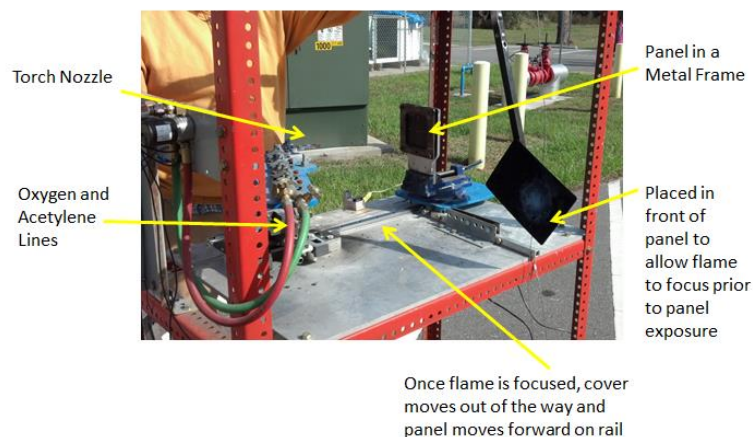


Figure 9. Torch Test Setup

Figure 10 shows the results of the polysiloxane panels, which only had one pyrolysis cycle and no reinfiltration. Burnthrough occurred around 30-35 seconds into the test. The maximum

temperature that was seen by the back face prior to burn through was 180°C. LBF106 and LBF107 had the thermocouple slightly off center, which gave lower values but still followed the general trend. Figure 11 shows an example of a panel after testing. The front of the panel shows melting and ablation due to the flame. From the back of the panel, a small hole is shown where burnthrough occurred; the region around the hole is melted adhesive that was used to hold on the thermocouple. The side of the panel shows delamination.

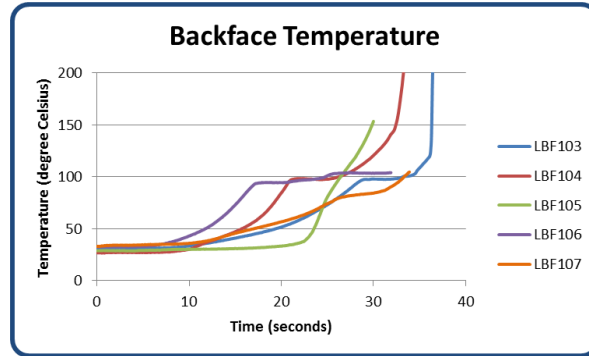


Figure 10. Torch Testing Results of the Polysiloxane Panels

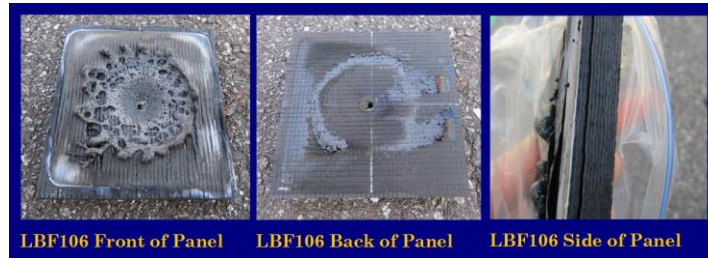


Figure 11. Panel LBF106 Post Test

Figure 12 shows the results for the first set of polycarbosilane panels, which had only one pyrolysis cycle and no reinfiltration. Only one of the five panels tested burned through; it took 40 seconds and reached a backface temperature of 500°C. The other panels were tested until the adhesive holding on the thermocouple melted. Because these panels were slightly bowed, there may have been heat intruding between the metal frame and the panel, which allowed the heat to the back of the panel from the sides. Also, because the panels bowed outward, the impingement point was slightly closer than 3/4" which may have changed the heat flux seen by the front of the panel. Even with the early termination, the testing continued for 40-60 seconds, lasting longer than the polysiloxane panels. Figure 13 shows the panel which did burn through. These panels cracked through the thickness very early into the test (can be seen in the back face and side views), and the ablation appears to be slightly different than what was seen with the polysiloxane panels. This is most likely due to the bowing in the panel.

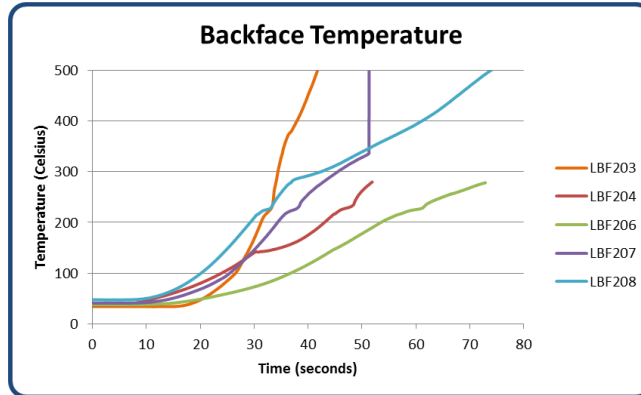


Figure 12. Torch Testing Results of the Polycarbosilane Panels Set 1



Figure 13. Panel LBF203 Post Test

Figure 14 shows the results for the second set of polycarbosilane panels, which underwent reinfiltration as shown in Table 7 above. LBF216 cracked immediately due to the sudden stop of the frame as it slid forward on the rail towards the torch nozzle. The other panels cracked toward the end of the test. Figure 15 shows one of the panels after the torch test. These panels had burnthrough times of 10-13 seconds, which is much less than the first set of panels, although the condition of these panels appears similar to the condition of the first set of panels. The decreased burnthrough time could have been a result of the change in the fabric form (the first set was biaxial, the second set was plain weave), or it could have been due to the interface between the fiber and the matrix. Changes in the test setup, such as how the thermocouple was applied to the back of the panel and possible a slight change in the heat flow from the torch, could have also affected the results.

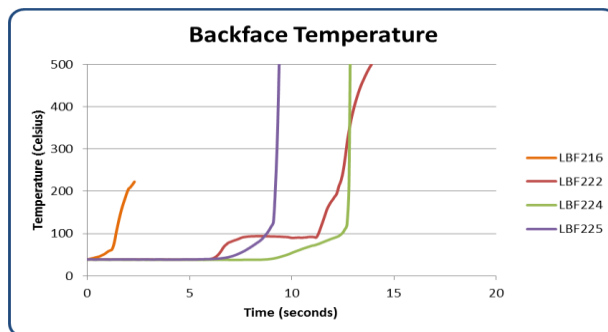


Figure 14. Torch Testing Results of the Polycarbosilane Panels Set 2

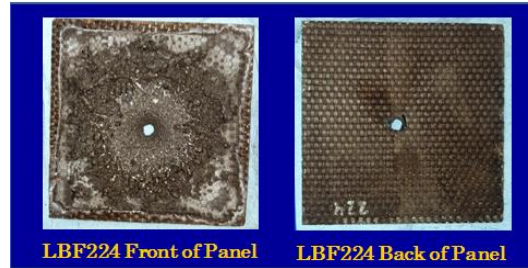


Figure 15. Panel LBF224 Post Test

4. CONCLUSIONS

Ceramic matrix composites are becoming available in more forms. By using a polymer derived ceramic, panels can be fabricated, cured, and then pyrolyzed to obtain a ceramic matrix in a bulk, structural component. Basalt fiber was chosen for reinforcement. The panels which underwent reinfiltration showed less flexural strength and had shorter burnthrough times during the torch test. This may be because of changes in the basalt fiber or changes in the bond between the fibers and the ceramic matrix. The SEM images show a better bond, which causes the fibers to break in a more brittle manner and does not increase the strength of the ceramic. More testing will be required to fully understand the phenomena taking place.

5. REFERENCES

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