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

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ABSTRACT

This research focuses on the development of a family of new ablative nanocomposite materials through a collaboration between The University of Texas at Austin, Techneglas, and Dyna-Tek. The DT-1116 resin system, based on polysiloxane chemistry was evaluated for potential for use in the next generation of thermal protection system (TPS) materials. TGA and microscale combustion calorimetry (MCC) were used to examine the thermal stability and flammability properties of polysiloxane resin system. These thermal properties were compared with two state-of-the-art (SOTA) resins: SC-1008 phenolic and PT-15 cyanate ester resins. The DT-1116 polysiloxane resin showed the highest char yield at 87%. The resin also showed the lowest heat release capacity (HRC) with 36 J/g-K. These data suggest that the polysiloxane resin has excellent properties for potential use in ablative materials.

1. INTRODUCTION

Ablative materials are widely used in the aerospace and defense industry. This class of material has unique properties, which allows them to resist the high heat flux environment experienced by spacecraft and rocket motors. Some of the most advanced thermal protection systems, vertical launching systems, and rocket motors contain ablative composites utilizing fiber reinforced SC-1008 phenolic ablative systems.

While many ablatives in use today consist of SOTA resins, such as SC-1008 and PT-15, there is a need for new ablative materials, which can withstand higher temperatures and heat fluxes. Better ablatives allow for weight-savings and better performance for advanced propulsion systems and thermal protection systems for reentry vehicles. Atmospheric entry probes can encounter very harsh reentry environments due to high speeds, such as the Galileo probe sent to Jupiter. It utilized thick carbon/phenolic TPS [1,2]. A report by NASA Ames after the mission determined that future missions to the planet, especially ones utilizing multiple probes, would require a "new, robust, and efficient TPS" [2]. The most recent development in ablative TPS materials by NASA has been 3D woven cyanate ester composites that act as both a compression pad and ablative heat shield for the new Orion spacecraft [3]. Stronger TPS ablatives can also minimize the amount of material needed to protect the primary structure of the rocket and involve less weight to the overall structure of the vehicle [2]. One resin system that is showing strong potential as a new TPS material is the DT-1116 polysiloxane based resin system.

We have been investigating material properties of four neat resins: SC-1008 phenolic, PT-15 cyanate ester, and two different formulations of DT-1116 polysiloxane resin system: DT-1116-1 and DT-1116-2. Experiments were carried out to compare the char yield, thermal stability, flammability, and kinetic parameters of each material. By analyzing the char yield of each material, it allows us to focus on an important part of the TPS's function, the creation of a protective char layer as it undergoes pyrolysis. As surface of the TPS begins to thermally degrade and form a porous char layer, it acts as a sacrificial layer, providing an extra layer of thermal insulation to the TPS until higher temperatures allow it to undergo oxidization or be removed by external forces from the hypersonic gas flow [4,5]. This char blocks heat and oxygen from reaching the virgin TPS material, while regulating the release of the cooling pyrolysis gases [4]. This study focuses on the development and characterization of new ablative materials that can be equal or exceed legacy materials utilizing SOTA resins. This study will evaluate the polysiloxane resin's potential for use as an ablative TPS material.

2. MATERIAL SYSTEMS

2.1 SC-1008 Phenolic Resin

SC-1008 is MIL-standard phenolic resole resin manufactured by Hexion [6]. It is the most commonly used resin for manufacturing ablative, such as carbon/phenolic (Cytec's MX4926N used for solid rocket motor nozzle), silica/phenolic (Cytec's MX2600 used for solid and liquid rocket motor nozzles), and in PICA. This phenolic resole resin has a char yield of 56%.

2.2 PT-15 Cyanate Ester Resin

PT-15 is a low viscosity cyanate ester (CE) resin manufactured by Lonza [7]. It is a common resin used for high-temperature application. This CE is very similar to the Tencate EX-1510 CE resin used by Feldman *et al.* 3D woven multifunctional ablative TPS for Orion [3, 8]. This cyanate ester resin has a char yield of 57%.

2.3 DT-1116 Polysiloxane Resin

DT-1116 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-Tek, LLC is the manufacturer and recently introduced a series of ceramic matrices specifically designed as a binders for composite material as flame shielding barriers. This system offers the uniqueness of a low temperature cure resin system that exhibits an extreme resistance to a high temperature environment. It also possesses properties, such as low thermal transfer, excellent chemical resistance, low to no smoke or toxic fumes when exposed to flame sources. These are fire, smoke, and toxicity (FST) characteristics that are desirable for fire resistant polymers. Two DT-1116-1 and DT-1116-2 resin systems are selected in this study have a char yield of 87% and 85%, respectively.

3. CHARACTERIZAITON METHODS

3.1 Char Yield Definition

In a recent char yield study conducted by Koo *et al.* [10], conditions were developed for char yield determination with standard test procedures based on the NASA PICA report [11]:

- Dry the TGA sample at 150^{o}C for 30 min.
- TGA sample size ~20mg.
- TGA heating rate of 20^{o}C/min in nitrogen.
- Char yield is defined as the mass remaining at 1,000^{o}C.

Several high-temperature commercially available resins have been examined in a comprehensive char yield study using TGA, dTGA, and T_d (decomposition temperature) [10]. The four resin systems used in this study, such as SC 1008, PT-15, DT-1116-1 and DT-1116-2 are selected from this ongoing char study by Koo *et al.* [10].

3.2 Thermal Stability and Kinetic Parameters Study

3.2.1 Thermal Stability Study

TGA experiments were conducted using four heat ratings of 5, 10, 20, and 40^{o}C/min under nitrogen to examine the thermal stability of the four resin systems using a TA Instruments Hi-Res TGA 2950 Thermogravimetric Analyzer. These TGA data were used to determine kinetic parameters using an isoconversion technique discussed in later section.

3.2.2 Kinetic Parameters and the Isoconversion Method

The rate of thermal decomposition of polymers can be modeled by the kinetic rate equation,

$$-\frac{1}{w_0}\frac{dw}{dt} = Af\left(\frac{w}{w_0}\right)^n \exp\left(-\frac{E}{RT}\right), \qquad [1]$$

Where A is the pre-exponential factor, E is the activation energy, n is the order of reaction, and $f(w/w_0)$ is an arbitrary function of instantaneous weight fraction.

To predict the thermal response of a polymer, accurate values of these kinetic parameters over the range of decomposition are required in a thermal model. TGA is a common polymer characterization technique to determine the thermal stability of a sample polymer by recording the weight change of the polymer as a function of increasing temperature or time at a constant rate. The multiple heating rate technique provides the activation energy, pre-exponential factor, and order of reaction over a wide a range of heating rates.

The isoconversion method is widely used to describe kinetics parameters [12]. The method can be summarized as follows. The rate of degradation is a function of temperature and solid conversion, X_s,

$$\frac{dX_s}{dt} = f(T, X_s) = k(A_s - X_s)^n \qquad [2]$$

Where X_s is defined as

$$X_s = \frac{w_0 - w}{w_0 - w_f} \qquad [3]$$

A_s is the maximum weight loss attainable at each temperature (value has been taken as 1.0), and k is the kinetic constant, which corresponds to the Arrhenius equation:

$$k = A\exp\left(-\frac{E}{RT}\right) \qquad [4]$$

A single-order reaction is used ($n = 1$), and the Ozawa-Flynn-Wall method [13] is considered, for obtaining the value of activation energy:

$$\ln\beta = \ln\left(\frac{AE}{R}\right) - 5.33 - \ln(1 - X_s) - 1.05\frac{E}{RT} \qquad [5]$$

Where β is heating rate. Plotting $\ln\beta$ as a function of $1/T$, linear equations can be used to fit each parametric value of X_s to obtain the values of activation energy and pre-exponential factor. These kinetic parameters imply that the thermal decomposition of the polymer can be expressed by a simple kinetic equation with single effective values of A and E. By adjusting the order of reaction, a separate set of kinetic parameters can be obtained, but when plotting $\log A$ as function of E, a linear curve fit can be observed using different values of n, which is result of the kinetic compensation effect.

3.3 Microscale Combustion Calorimeter

Thermal combustion properties were measured using a Microscale Combustion Calorimeter (MCC2, Govmark, Inc.) according to ASTM D7309-2007 (Figure 1). MCC directly measures heat release parameters of small amounts of materials in the size of several milligrams. The heat release rate during combustion and the total heat release are calculated by oxygen consumption rate and integration of the heat release rate versus time, respectively. The combustor temperature was held constant at 900°C, the pyrolyzer was heated from 100°C to 750°C and the heating rate of the sample in the pyrolysis zone was 1°C/sec. Each formulation was tested for 3 repetitions to calculate error bars.

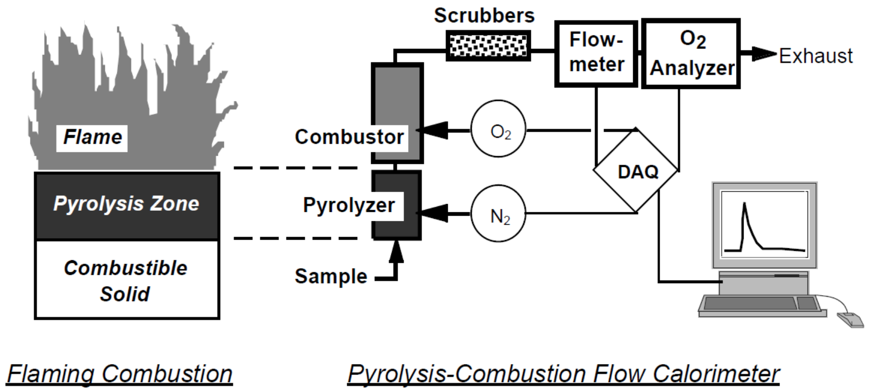


Figure 1. Illustration of Microscale Combustion Calorimeter [14].

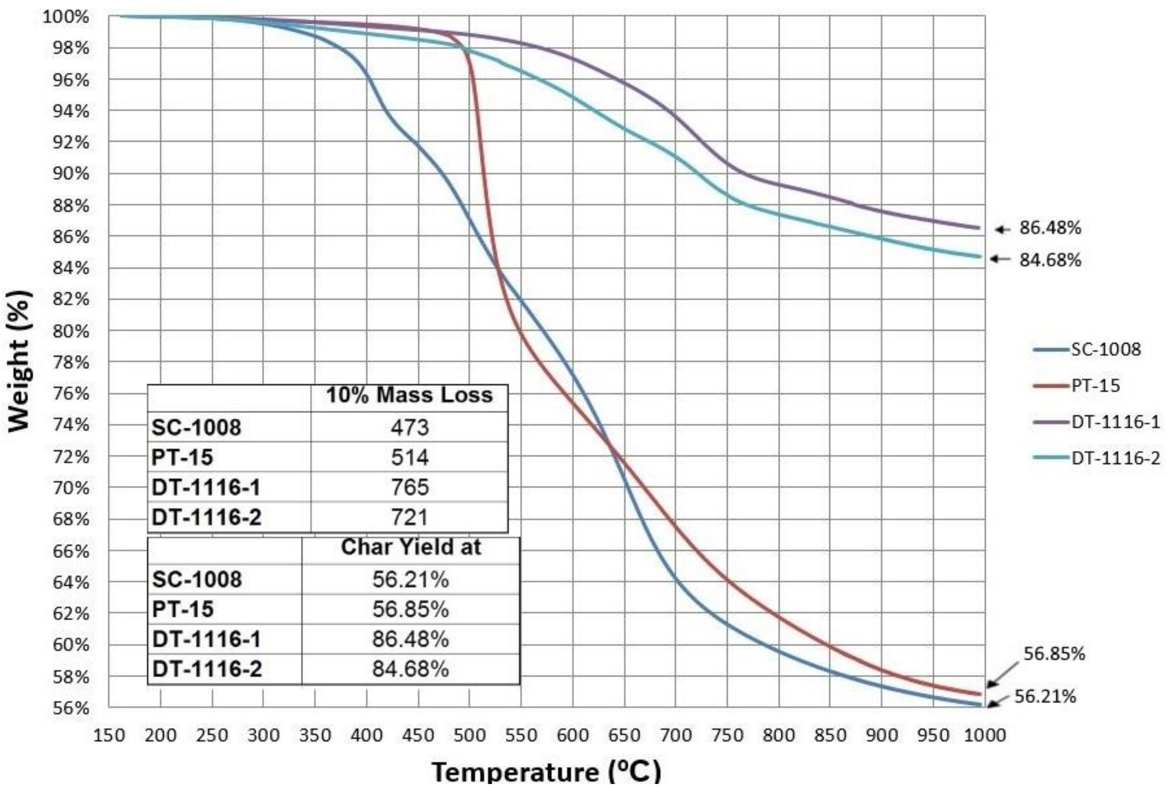
4. DISCUSSION OF RESULTS

4.1 Char Yield Results

The "char yield" was measured using a TA Instruments Hi-Res TGA 2950 Thermogravimetric Analyzer with a material sample size of 20 mg. The samples were dried using an isothermal (constant temperature) at 162.7ºC (325ºF) for 30 minutes in nitrogen. Then a heating rate of 20ºC/min from 162.7ºC to 1000ºC in nitrogen was applied. The initial weight (100% weight) was taken after the 30 minute drying. The char yield is defined as the weight % at 1,000ºC.

The char yield studies were performed on neat resin samples of SC-1008, PT-15, DT1116-1, and DT1116-2. Figure 2 shows the results of the char yield studies. The table in the figure shows the decomposition temperature (T_d) at 10% mass loss and the char yield at 1,000ºC. The following are the char yield results: SC-1008 = 56.21%, PT-15 = 56.85%, DT-1116-1 = 86.48%, and DT-1116-2 = 84.68%. Figure 3 shows the derivative of the TGA data, dTGA (%/ºC), for the four neat resins. The temperature of the peaks of the dTGA, T_d at 10% mass loss, and % weight at 1,000ºC are noted on the graphs.

From the Figure 3 of the dTGA result, SC-1008 shows three distinct reactions occur at 410, 497, and 655ºC, this resin system exhibits 3 transitions that are reported for phenolic resins [14]. PT-15 shows only one reaction occurs at 511ºC, suggesting a uniform decomposition for this resin system. DT-1116-1 shows two distinct reactions occur at 722 and 873ºC. DT-1116-2 shows four distinct reactions occur at 496, 532, 627, and 725ºC. It was verified with the manufacturer that there are several fillers in this resin systems. The DT-1116-1 resin also has the highest T_d at 10% mass loss (765ºC) amongst these four resin systems As a result, the DT-1116-1 resin is the ideal candidate to be selected for further studies.



	10% Mass Loss
SC-1008	473
PT-15	514
DT-1116-1	765
DT-1116-2	721

	Char Yield at
SC-1008	56.21%
PT-15	56.85%
DT-1116-1	86.48%
DT-1116-2	84.68%

Figure 2. Char yield results for SC-1008, PT-15, DT1116-1, and DT1116-2.

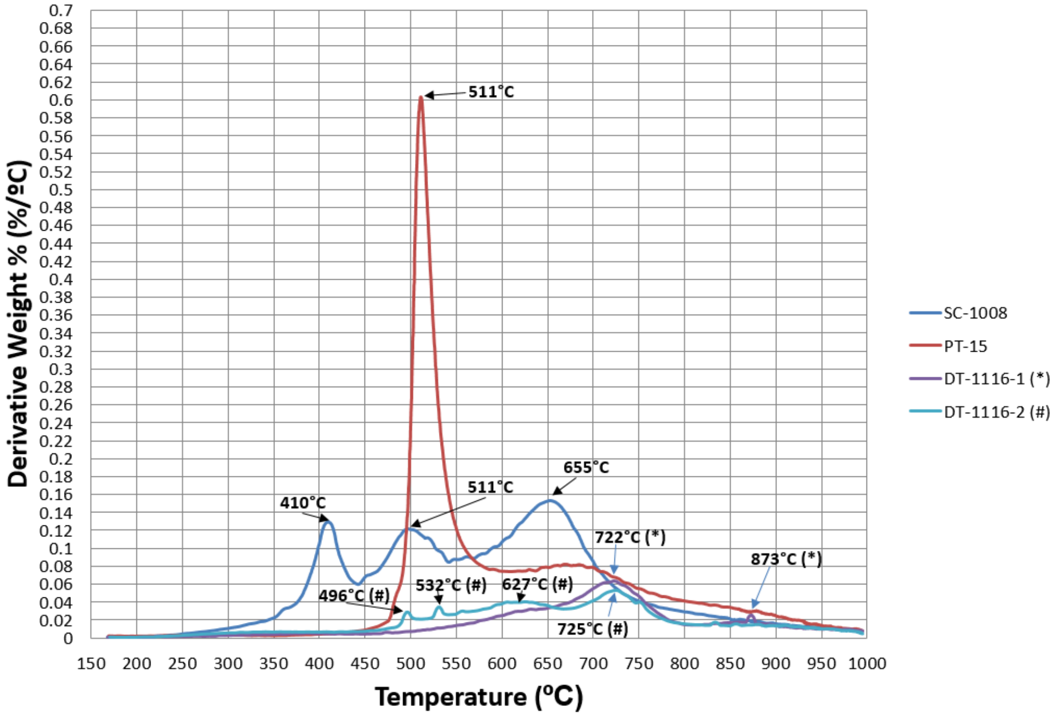


Figure 3. dTGA (%/ºC) data for SC-1008, PT-15, DT1116-1 (*), and DT1116-2 (#).

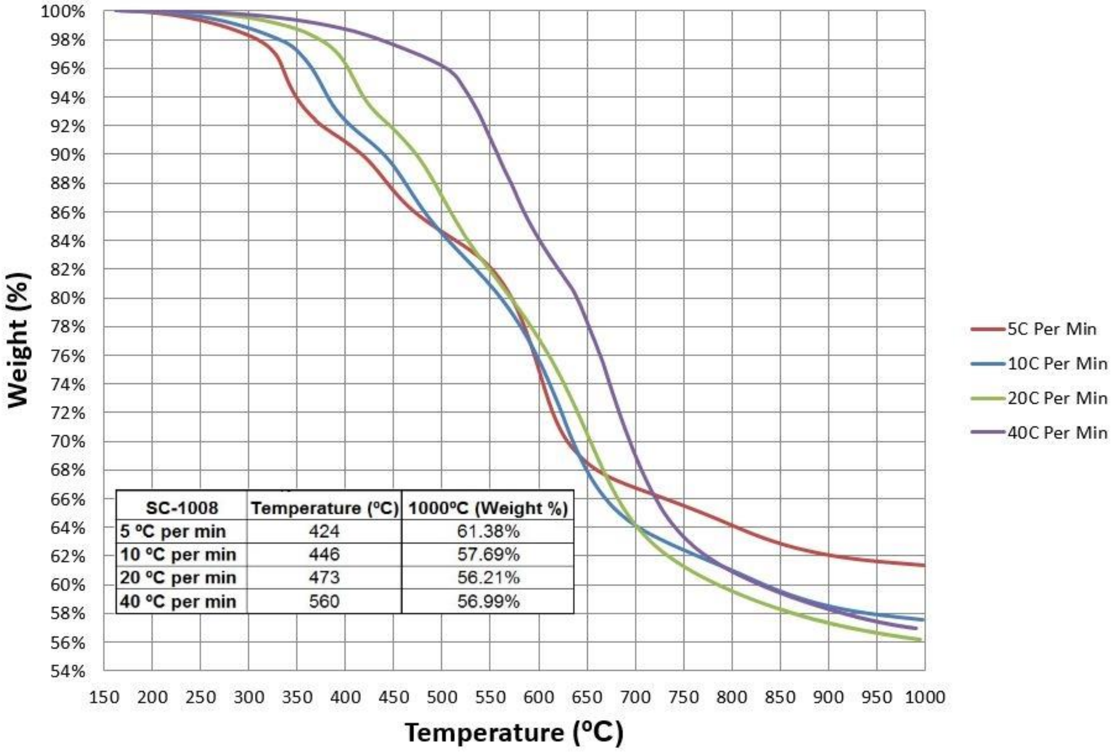
4.2 Thermal Stability and Kinetic Parameter Results

The thermal stability studies were performed on neat resin samples of SC-1008, PT-15, DT1116-1, and DT1116-2. Figures 4 to 7 show the neat resins with the four heating rates of 5, 10, 20, and 40 ºC/min.

From Figure 4, it is observed in general the residual mass of SC-1008 decreases from 61% to 57% as the heating rate increases; while the T_d of 10% mass loss increases from 416 to 557ºC. From Figure 5, it is observed the residual mass of PT-15 decreases from 61% to 55% as the heating rate increases; while the T_d of 10% mass loss increases from 474 to 550ºC. From Figure 6, it is observed the residual mass of DT-1116-1 stays relatively stable at 5, 10, and 20ºC/min at 86% and increases slightly to 90% at 40ºC/min. This phenomenon is very unusual. The T_d of 10% mass loss increases from 690º (at 1,000ºC) to 990ºC (at 990ºC), an increase of 300ºC! Further study is warranted to understand this unusual behavior. From Figure 7, it is observed the residual mass of DT-1116-2 stays relatively stable about 85 to 86% at the four heating rates; while the T_d of 10% mass loss increases from 688º to 781ºC, an increase of about 100ºC.

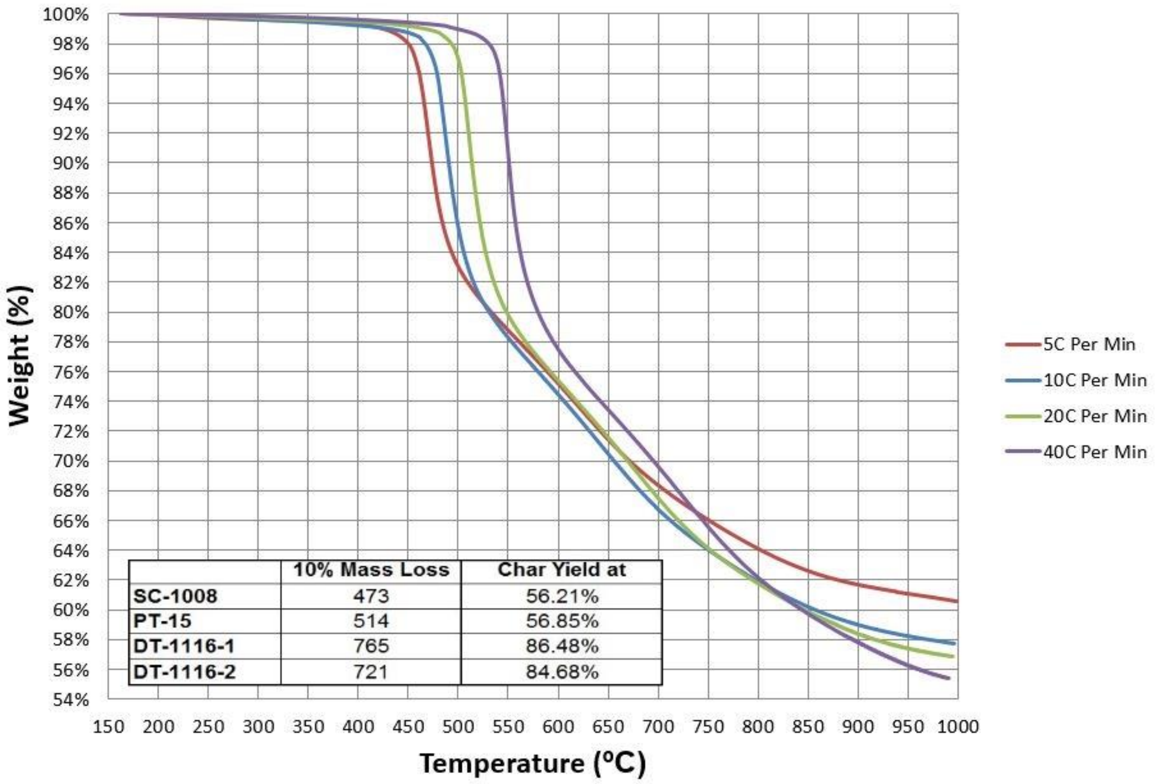
The T_d of 10% mass loss and weight percent at 1,000ºC for the four heating ratings are shown in tables in Figures 4 to 7 of each resin system. Table 1 shows a comparison of the T_d of 10% mass loss (ºC). Table 2 shows a comparison of the weight % at 1,000ºC at heating rates of 5, 10, 20, and 40ºC/min.

From the above analyses, DT-1116 resin shows an unusual behavior of increasing in residual mass as the heating rate increases from 5 to 40ºC/min while the SC-1008 and PT-15 show the opposite trend. The T_d at 10% mass loss of DT 1116-1 shows an increase of 300ºC. Again, the DT-1116-1 resin is the ideal candidate to be selected for further studies.



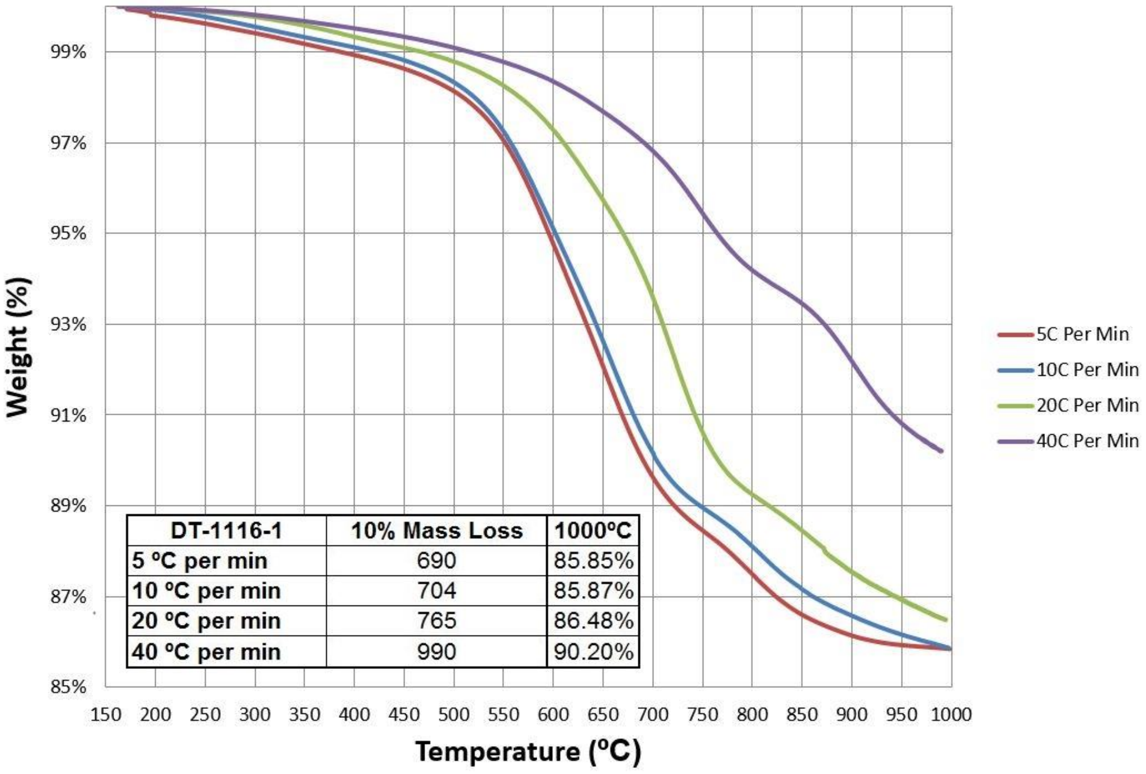
SC-1008	Temperature (ºC)	1000ºC (Weight %)
5 ºC per min	424	61.38%
10 ºC per min	446	57.69%
20 ºC per min	473	56.21%
40 ºC per min	560	56.99%

Figure 4. SC-1008 phenolic resin at heating rates of 5, 10, 20, and 40ºC/min.



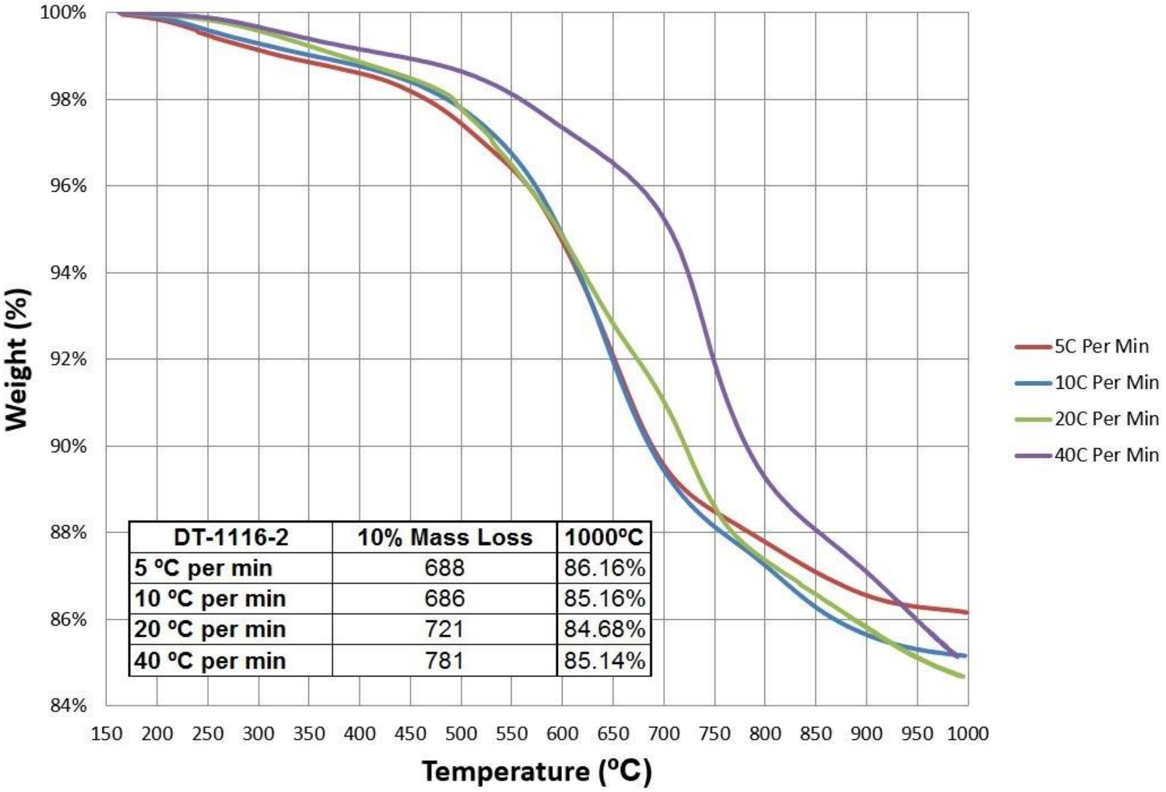
	10% Mass Loss	Char Yield at
SC-1008	473	56.21%
PT-15	514	56.85%
DT-1116-1	765	86.48%
DT-1116-2	721	84.68%

Figure 5. PT-15 cyanate ester resin at heating rates of 5, 10, 20, and 40ºC/min.



DT-1116-1	10% Mass Loss	1000ºC
5 ºC per min	690	85.85%
10 ºC per min	704	85.87%
20 ºC per min	765	86.48%
40 ºC per min	990	90.20%

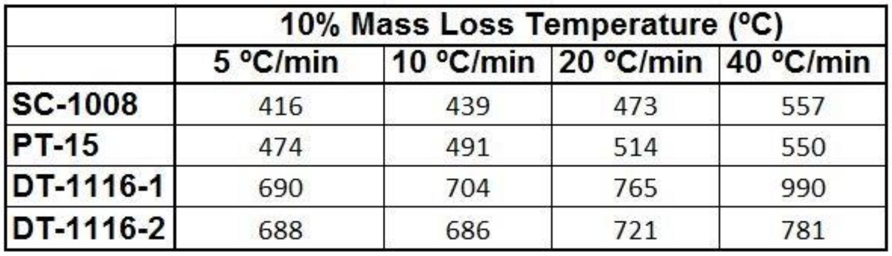
Figure 6. DT-1116-1 polysiloxane resin at heating rates of 5, 10, 20, and 40ºC/min.



DT-1116-2	10% Mass Loss	1000ºC
5 ºC per min	688	86.16%
10 ºC per min	686	85.16%
20 ºC per min	721	84.68%
40 ºC per min	781	85.14%

Figure 7. DT-1116-2 polysiloxane resin at heating rates of 5, 10, 20, and 40ºC/min.

Table 1. Decomposition temperature (T_d) of 10% mass loss temperature at heating rates of 5, 10, 20, and 40ºC/min.



	10% Mass Loss Temperature (ºC)			
	5 ºC/min	10 ºC/min	20 ºC/min	40 ºC/min
SC-1008	416	439	473	557
PT-15	474	491	514	550
DT-1116-1	690	704	765	990
DT-1116-2	688	686	721	781

Table 2. Weight % at 1,000ºC at heating rates of 5, 10, 20, and 40ºC/min.

	Weight % at 1000ºC			
	5 ºC/min	10 ºC/min	20 ºC/min	40 ºC/min
SC-1008	61.38%	57.54%	56.21%	56.99%
PT-15	60.61%	57.69%	56.85%	55.44%
DT-1116-1	85.85%	85.87%	86.48%	90.20%
DT-1116-2	86.16%	85.16%	84.68%	85.14%

4.3 Flammability Properties

Flammability properties are characterized by MCC tests. MCC, developed by FAA, is a small sample test which measures the heat release rate of milligram sized samples. It is a convenient tool to screen material's flammability properties [14].

The typical MCC heat release curves of the four resins are plotted in Figure 8. DT1116-1 and DT1116-2 have very similar heat release behaviors, both sample have PHRR at around 630°C and their HRR curves show good agreement with each other throughout the entire heating range. Judged by the trend of the heat release curves of DT1116-1 and DT1116-2 at 750°C, there may be another heat release peak above 750°C. More investigation in the future is needed to confirm this observation. PT15 has one major HRR peak at 455.9°C. The PHRR of PT15 is significantly higher than the other 3 resins indicating its relatively poor flame resistant properties. SC1008 have three distinct HR peaks, the overall HRR values are also higher than that of DT1116-1 and DT1116-2.

Calculated from MCC data, heat release capacity (HRC) is an intrinsic material property independent of heating rate and sample size [15]. The HRC comparison of the four resin systems are shown in Figure 9. DT1116-1 and DT1116-2 have identical HRC of 36 J/g-K. On the other hand, because of the high PHRR of PT15, a much higher HRC of 159.3J/g-K is not surprising. SC1008 has HRC of 53.3J/g-K which is 48% higher HRC than that of DT1116-1 and DT1116-2.

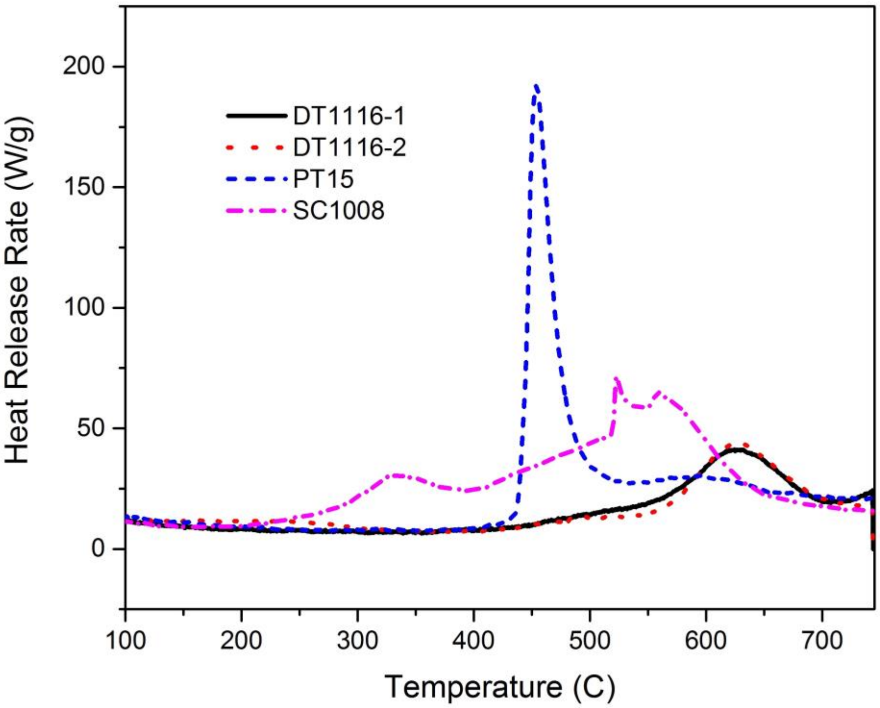


Figure 8. Typical heat release curves for the four resin systems.

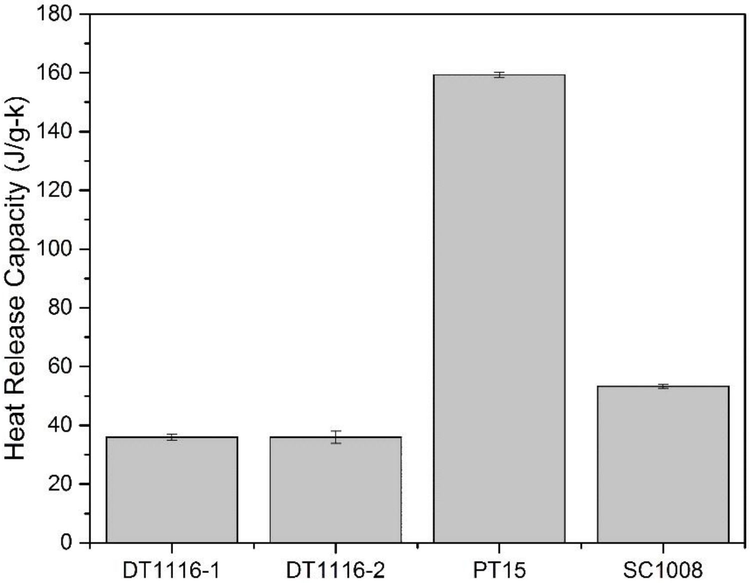


Figure 9. Comparison of the Heat Release Capacities for the four resin systems.

5. SUMMARY AND CONCLUSIONS

5.1 Summary

The polysiloxane based resin system has shown superior char yield, thermal stability, and flammability properties. The char yield study showed that DT-1116 polysiloxane resins possessed the highest char yield. DT-1116-1 exhibited the best results with 87% char yield. An increase of 54% in char yield was determined as compared to the phenolic resin and the cyanate ester resin. The study also revealed that as the heating rates were increased, the DT-1116-1 produced higher residual masses, whereas the other three resins resulted in lower residual masses. The DT-1116-1 also showed better thermal stability and char yield than the DT-1116-2, with the dTGA revealing a number of additional reactions occurring at lower temperatures in the DT-1116-2 resin. However, the heat release curve for both DT-1116 resins were nearly identical with a HRC of 36 J/g-K. SC-1008 phenolic's HRC was 48% higher at 53.31 g-K and PT-15 cyanate ester's HRC was 443% higher at 159.33 g-K. Due to the multiple stage degradation and the high residual mass of the polysiloxane resins, the activation energy could not be accurately determined with the current models. A better model is needed. The DT-1116-1 resin is selected to further study.

5.2 Future Studies

Because ablative materials are typically fiber-reinforced composites, the new resin system will be used to impregnate fibers to create ablative test samples. Silica fabric will be used to create DT-1116/silica composites. Experiments will be conducted to determine the optimal ratio of resin: fiber for ablation resistance. It is also planned to investigate the creation of nanocomposite ablatives by incorporating different amounts of nano-silica into the DT-1116. These candidate materials then can be evaluated in an oxy-acetylene test bed (OTB) at a high heat flux (1,000 W/cm^2) of a specified test duration to simulate a re-entry environment. Advanced diagnostics, such as two-color IR pyrometer, in-depth thermocouples, high definition video camera, and IR video camera will be setup for each ablation testing experiment to analyze the thermal and ablation performance. The investigation of the activation energy using a model which can account for its high char yield and multiple stage of polymer decomposition is being considered.

6. ACKNOWLEDGMENTS

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7. REFERENCES

1. B. Laub, E. Venkatapathy, E., "Thermal Protection System Technology and Facility Needs for Demanding Future Planetary Missions." *International Workshop on Planetary Probe Atmospheric Entry and Descent Trajectory Analysis and Science*. Lisbon, Portugal, 6-9 Oct. 2003, Retrieved 5-31-2015.

2. F. S. Milos, "Galileo Probe Heat Shield Ablation Experiment," *Journal of Spacecraft and Rockets*, 34 (6), (1997): 705-713J.

3. J. Feldman *et al.*, "Development of a 3D Multifunctional Ablative Thermal Protection Systems for Orion," *National Space & Missile Materials Symposium*, Chantilly, VA, June 22-25, 2015.

4. L. Torre, J. M. Kenny, and A. M. Maffezzoli, "Degradation behaviour of a composite material for thermal protection systems Part I–Experimental characterization," *Journal of Materials Science*, 33 (12), (1998): 3137-3143
5. R. A. Vaia *et al.*, "Polymer/layered silicate nanocomposites as high performance ablative materials," *Applied Clay Science*, 15(1), (1999): 67-92.
6. Hexion technical datasheet of SC-1008 phenolic resole resin.
7. Lonza technical datasheet of PT-15 cyanate ester resin.
8. J. Feldman *et al.*, "Development of an Ablative Quartz/Cyanate Ester Composite for the Orion Spacecraft Compression Pad," *Proc. CAMX 2015,* Dallas, Oct 24-28, 2015.
9. Dyna-Tek technical datasheet, Kansas City, MO (www.dyna-tek.com), accessed Jan 2016.
10. J. Koo *et al.*, "Char Yield Studies of Several High-Temperature Resin Systems for Ablative Thermal Protection Systems," unpublished data, Feb. 2016.
11. "PICA Material Property Report C-TPSA-A-DOC-158" for Crew Exploration Vehicle Block II Heatshield Advanced Development Project, NASA Report, Rev. 1, June 8, 2009, ITAR report received from NASA-Johnson Space Center, Houston, TX.
12. J. Ceamanos, J. F. Mastral, A. Millera, and M. E. Aldea, "Kinetics of pyrolysis of high density comparison of isothermal and dynamics experiments," *J. of Analytical and Applied Pyrolysis*, 65(2), 2002: 93-110.
13. M. Day, and D. R. Budgell, "Kinetics of thermal degradation of poly(phenylene sulfide)," *Thermochimica Acta*, 203, (1992): 465-474.
14. A. Knop and L. A. Pilato, "Phenolic Resins: Chemistry, Applications and Performance, Future Directions," Springer-Verlag, Berlin, 1985, pages 140+.
15. R. E. Lyon, R. Walters. *A Microscale Combustion Calorimeter*. DOT/FAA/AR-01/117, Office of Aviation Research, Washington, DC, Final Report, Feb 2002.