Fracture in Phenolic Impregnated Carbon Ablator

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The thermal protection materials used for spacecraft heat shields are subjected to various thermal-mechanical loads during an atmospheric entry which can threaten the structural integrity of the system. This paper describes the development of a novel technique to understand the failure mechanisms inside thermal protection materials. The focus of research is on the class of materials known as Phenolic Impregnated Carbon Ablators (PICA). PICA has successfully flown on the Stardust spacecraft and is the TPS material chosen for the Mars Science Laboratory (MSL) and SpaceX Dragon spacecraft. Although PICA has good thermal properties, structurally, it is a weak material. In order to thoroughly understand failure in PICA, fracture tests were performed on FiberForm®* (precursor of PICA), virgin and charred PICA materials. Several samples of these materials were tested to investigate failure mechanisms at a microstructural scale. Stress-strain data were obtained simultaneously to estimate the fracture toughness. It was found that cracks initiated and grew in the FiberForm when a critical stress limit was reached such that the carbon fibers separated from the binder. However, both for virgin and charred PICA, crack initiation and growth occurred in the matrix (phenolic) phase. Both virgin and charred PICA showed greater strength values compared to FiberForm coupons, confirming that the presence of the porous matrix helps in absorbing the fracture energy.

I. Introduction

Fracture in any system is a catastrophic event that system designers try to prevent. In spacecraft heat shields, it is of paramount importance as safety of the crew members and success of the mission is at stake, and it affects the planning for future missions. The Columbia disaster occurred due to mechanical damage to the thermal protection system (TPS) that could not survive the heating during re-entry[1]. However, the study and analysis work involved with thermal protection materials is very complex. Many factors contributing to this complexity are: porosity of thermal protection materials, temperature dependent mechanical and physical properties, and a combination of thermal and mechanical loads at various points in the trajectory. While arc-jet and other thermal-mechanical tests provide some understanding regarding the survivability of TPS materials[2,3], an in-depth systematic studies of fracture toughness and failure mechanisms are required to optimize materials and predict the failure in TPS when subjected to a combination of thermal-mechanical loads. Some researchers in past, have investigated the fracture characteristics of ceramic thermal protection tiles, used in Space Shuttle[4,5], however, to the authors knowledge there has not been extensive research performed to study fracture toughness and failure mechanisms at a microstructure scale in ablating TPS materials. The research discussed in this paper is one of the first attempts to investigate failure mechanisms in ablators at a micro-structural scale and provide an understanding that may lead to the development of

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structurally stronger materials. The present work focuses on investigating the failure mechanisms in Phenolic Impregnated Carbon Ablator (PICA).

PICA is a logical choice for this research because it was the material used on the Stardust probe[6] and will be used in the heat shield for the Mars Science Lab (MSL)[7] mission and on the SpaceX Dragon spacecraft[8]. PICA was developed by scientists at NASA Ames in 1996[9]. Although PICA has very good thermal properties, structurally it is a weak material, posing a challenge for the system designers to use it in the presence of mechanical loads and severe stresses. Several development efforts are underway to improve the structural properties of PICA without compromising the thermal properties or significantly increasing the density. The researchers at NASA Ames and Fiber Materials Incorporated (FMI) have been changing process parameters to alter the microstructure to improve mechanical properties[10,11,12]. In order to optimize the microstructure it is important to understand mechanisms of crack initiation and propagation at a microstructure scale. In the present research the mechanical tests were performed on FiberForm (precursor of PICA), virgin and charred PICA and crack propagation was investigated at a microstructure scale in each case. These tests also provided the data for estimation of fracture toughness, which can be later used for modeling of fracture as well as development of micromechanical failure models. The next section describes the microstructure of FiberForm, virgin, and charred PICA. Section III and IV discuss the instrumentation and specimen design. Section V describes the test data and results. Summary and conclusions are provided in section VI.

II. Microstructure

A. Fiberform

FiberForm is a low density very porous carbon fiber insulation material designed for high temperatures applications. It is processed at Fiber Materials Incorporated (FMI) and is the precursor substrate for processing PICA. Micrographs of FiberForm at different magnifications are shown in Figure 1. It consists of a group of carbon fibers bonded to each other by means of an organic binder that is carbonized at very high temperature. After carbonization, all the organics evaporate and only a thin carbonaceous phase remains as the binder that holds the fibers together. The binder concentration varies and, in some places, there are smaller concentrations while in other places there is a fairly large group of fibers bound together. Some cross-linking that joins the fibers together and makes it a rigid preform also takes place during the processing. Each individual strand of carbon fiber consists of 5-6 individual fibers of diameter 5-6 um that are joined together as shown in the higher magnification micrograph of Figure 1. The carbon fibers in FiberForm are oriented preferentially in one plane, as a result of the manufacturing process, making it a transverse isotropic material with different material properties in through-the-thickness (TTT) and in-plane (IP) directions. The IP strength and stiffness of FiberForm is significantly higher compared to the TTT direction. This material was tested first in the in-plane direction to obtain tensile strength and understand the failure mechanism.

B. Virgin PICA

As the name suggests, PICA is made by impregnation of phenolic resin within the FiberForm, followed by a cure cycle at an elevated temperature. It could be viewed as a two phase material consisting of a network of carbon fibers and a very porous phenolic matrix dispersed on and in-between the fibers as shown in Figure 2. This highly porous structure makes it a low density ablator. Due to the preferential orientation of carbon fibers in the FiberForm, PICA also displays the transverse isotropic behavior with significantly higher strength and stiffness in the in-plane direction compared to TTT direction.

C. Charred PICA

Ablative TPS materials are subjected to very high heat flux during atmospheric re-entry causing them to pyrolyze and char. In order to understand the effects of phase changes due to pyrolysis, two types of charred PICA materials, furnace charred and arc-jet charred PICA were studied. Furnace charred PICA samples were created by heating the specimens in a tube furnace to 1300^0C in inert environment. All the specimens were heated until they were uniformly charred. While all the organic material from the phenolic resin was evaporated, a thin carbonaceous matrix phase

was still present between the carbon fibers. The arc-jet charred PICA samples were prepared by cutting the upper charred PICA layer of post arc-jet test samples. Micrographs of both arc-jet and furnace charred PICA materials are shown in Figure 3a and 3b, respectively. Both materials show the presence of porous and thin carbonaceous matrix phase dispersed between the carbon fibers. However, in the arc-jet charred PICA the matrix on the top char layers is sparser compared to the furnace charred PICA. This is caused by the oxidation in arc-jet environment. This phenomenon was also observed in the PICA char on the Stardust reentry probe[13].
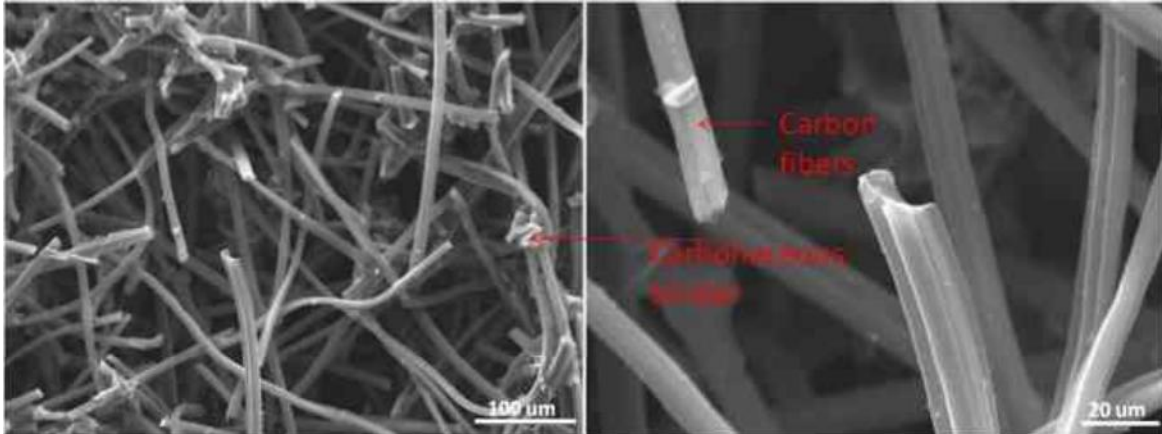
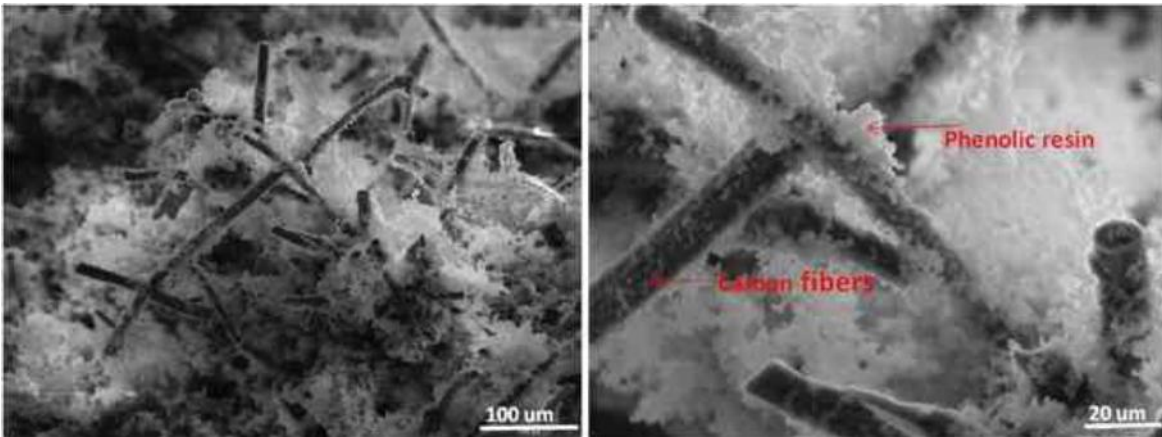**Figure 1: Micrographs of FiberForm at different magnifications.**

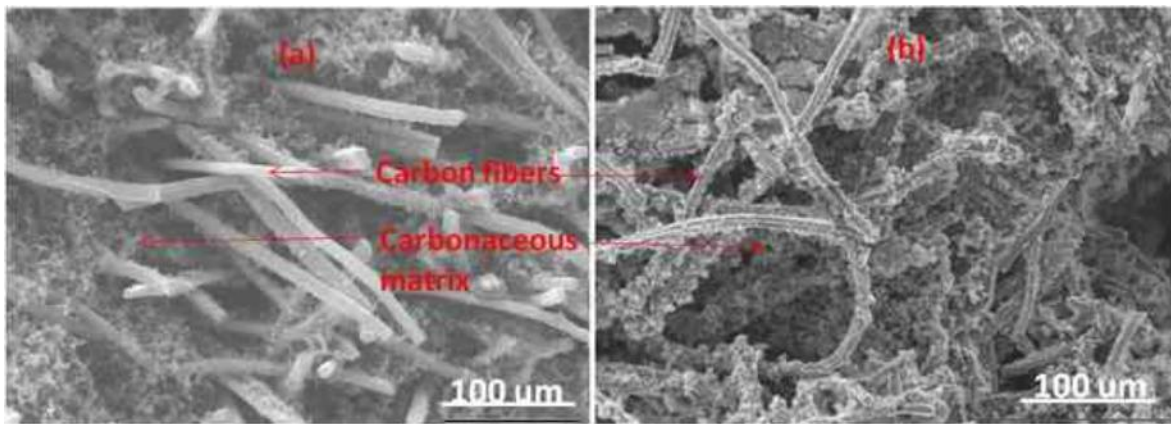**Figure 2: Micrographs of PICA at different magnifications.**

Figure 3: Micrographs of a) arc-jet char and b) furnace charred PICA.

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III. Experiment Design and Equipment

The experiments were performed inside a Philips XL-30 electron microscope unit from FEI (Fig. 4). A miniature custom designed mechanical stage was mounted inside the microscope chamber as shown in Figure 5. A data acquisition system was integrated to the stage to acquire stress-strain data during the tests. The mechanical sub-stage was driven by a small motor and could exert a tensile or compressive load of up to 5 kN on a suitable test specimen. A strain transducer was mounted on the stage that provided the displacement measurements. The stage can accommodate a range of samples with dimensions varying from 20.0 mm to 60.0 mm in length, 5.0 mm to 15.0 mm in width and 0.01 mm to 6.0 mm in thickness. These dimensions are ideal to obtain preliminary mechanical properties data for an experimental material.

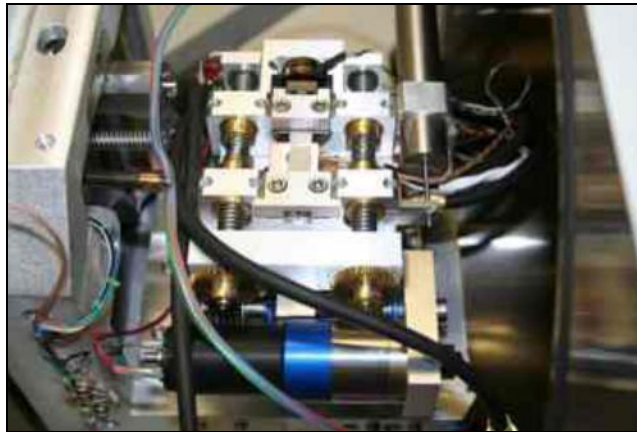**Figure 4: Experiment set-up for in-situ SEM fracture experiments**

Figure 5: Close up of the mechanical sub-stage

IV. Specimen Design

Small samples of dimension 5.7 cm x 1.0 cm x 0.38 cm were cut from a single PICA billet and FiberForm block. Sample dimensions and drawings are shown in Figure 6. To initiate fracture in a controlled manner and focus the electron beam to obtain high magnification micrographs, fine notches were cut into the samples at the midline, using a micro scriber tool. One of the notched charred PICA samples is shown in Figure 7. Specimens were fabricated with

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and without notches for each FiberForm, virgin and charred PICA materials to compare the stress-strain behavior and in-plane tensile strength. The notches were nominally 1.27mm to 2.54 mm in depth. The notch tip radius in most specimens was approximately 100 µm. These dimensions were sufficient to initiate crack at the notch tip and view the failure mechanisms in FiberForm and PICA. Thin aluminum tabs were glued to the ends of all the coupons with help of transfer coated RTV-560 (room temperature vulcanized) adhesive. This was required to avoid any local damage, slipping and premature failure of specimens near the grips.
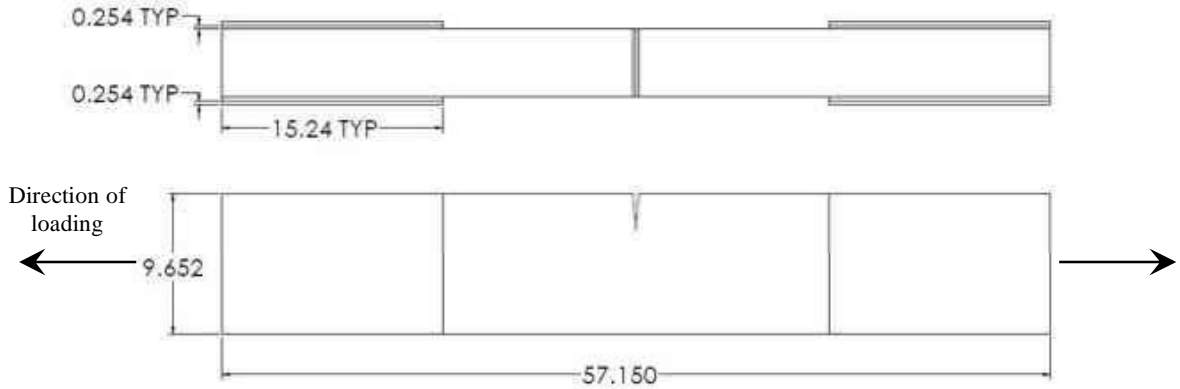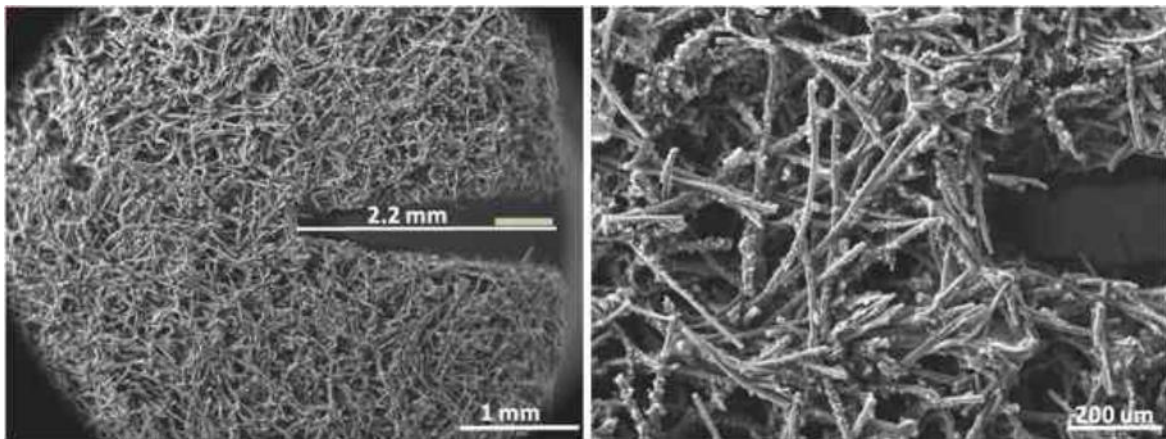

Figure 6: Specimen geometry (dimensions in mm).

Figure 7: Micrograph of a charred PICA coupon with a notch at different magnifications.

V. Test Results and Analysis

All the materials were tested at room temperature in the in-plane tension configuration as it is the stronger direction and it is easier to obtain the data. The samples were pulled inside the SEM chamber under high vacuum of 3.0e-04 mBar. To obtain quasi-static conditions, the samples were pulled at a rate of 0.1 mm/sec. The secondary electron mode detector was used to obtain high quality micrographs. For notched samples, the electron beam was focused at the notch tip prior to tests. Several micrographs were obtained near the notch tip prior to test in order to create a complete map near the notch at magnifications ranging from 25X-100X. A video camera was connected to the microscope to capture the fracture in real time (30 frames/sec). When a specimen was fractured, micrographs at various magnifications were obtained to observe the crack initiation and growth. Stress–strain data from the load cell and strain transducer were obtained at the same time using the data acquisition system. Some of the coupons were tested without notches to create a uniform uniaxial tension test configuration. While the primary objective of in-situ SEM testing was to observe the failure mechanisms inside the TPS material, the stress-strain data obtained during these tests helped in understanding the influence of material flaws on the stress-strain relationship. For some materials, like charred PICA, there are no tension test data available. The tension tests described here helped to

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obtain the in-plane tensile strength and toughness of charred PICA materials. The in-plane strength data for FiberForm, virgin, and charred PICA obtained during the tests, were compared with the configuration managed (CM) Crew Exploration Vehicle (CEV) TPS Advanced Development Project (ADP) material properties database values[14] to validate the tests and establish accuracy.

A. FiberForm Fracture Tests

Fracture tests were performed on both notched and un-notched FiberForm samples. The dimensions were kept constant across the samples to obtain consistent results. A 450N load cell was used for these tests because it provides more accurate information for smaller magnitude loads. For all the specimens with notches, cracks initiated and grew near the tip of notch. All the specimens fractured in a brittle manner as soon as they reached a critical tensile stress. The crack initiation was captured on video. Figure 8 shows the crack initiation near the notch tip in one of the specimens. By examining the videos and comparing pre-test versus post test micrographs, it can be seen that when the specimens reached a critical stress magnitude, the carbon fibers were pulled away from the binder where it was in smaller concentration. Figure 9 shows the loss of binder material and Figure 10 shows micrograph of fiber separation near the binder phase. Figure 11 also shows a magnified view of broken carbonaceous binder. Fiber breaking was not observed in any of the specimens. The tensile strength values and stress-strain data for representative un-notched and notched FiberForm coupons are shown in Figure 12. All the specimens fractured in the range of 400-600 KPa stress magnitude and presence of notches did not make a significant difference in tensile strength. This phenomenon is very different from traditional dense material and it will be important to take this into account when modeling fracture behavior of porous material. The stress-strain curves obtained for these samples also suggested nonlinear stress-strain behavior from the very beginning. For most specimens, the strain-to-failure was between 0.6%-1.0%. The strength data is comparable to the data obtained on FiberForm in the CM database for the Orion program[14].
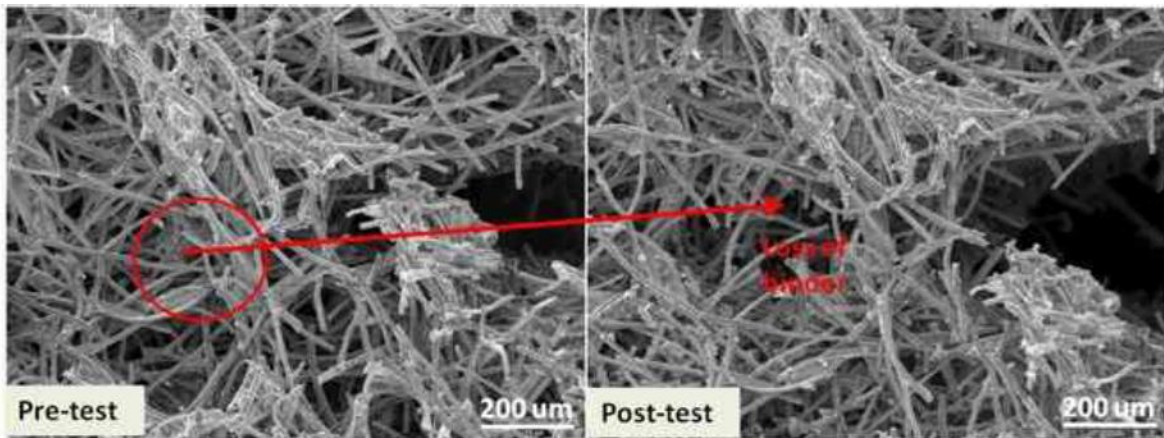
Figure 8: Crack initiation in FiberForm.

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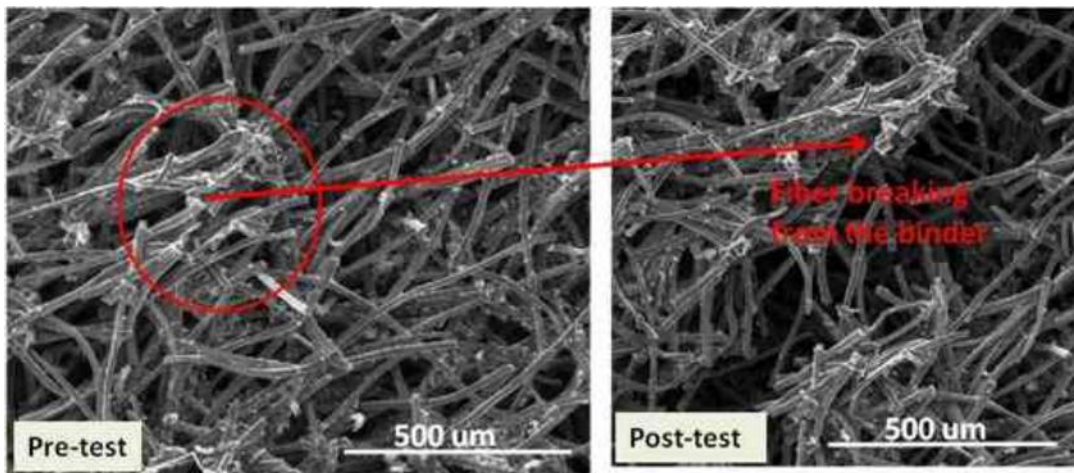**Figure 9: Loss of binder where it is sparser.**

Figure 10: Fiber separation near the binder.

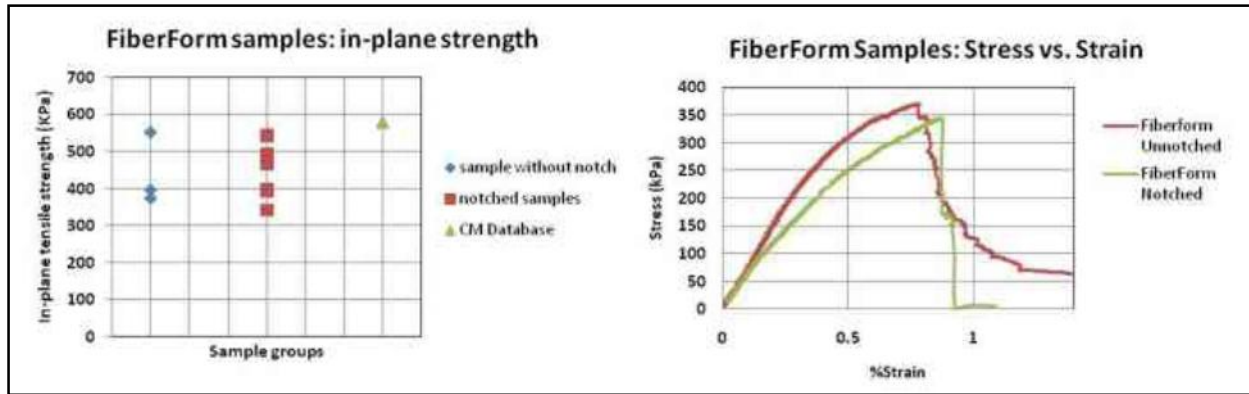**Figure 11: Magnified view of broken binder in FiberForm specimen.**

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Figure12: In-plane tensile strength and stress-strain data for FiberForm specimens.

B. Virgin PICA Fracture Tests

Fracture tests were performed on both notched and un-notched virgin PICA samples. The dimensions were kept constants across the samples to obtain consistent results. Specimens were fabricated with two different notch sizes, 1.27 mm and 2.54 mm, to investigate the effects of flaw size on strength and mechanical behavior. Similar to FiberForm, PICA specimens also fractured in a brittle fashion. Once specimens were at the critical stress magnitude, initiation and progress of cracks was rapid. Videos and micrographs capturing the crack initiation and crack paths were obtained during the testing of multiple notched specimens. For notched PICA specimens, the cracks initiated in the porous matrix phase near the notch tip, as shown in Figure 13. It progressed further in the phenolic matrix phase. The crack paths were governed by the presence of voids in the phenolic matrix phase. At various locations, crack bridging by carbon fibers as well as carbon fiber pull-out was observed. One such example is shown in one of post test micrograph in Figure 14. Stress-strain data were obtained for all the specimens. The tensile strength values for various notched and un-notched samples, as well as representative stress-strain plot for un-notched and 2.54 mm notched PICA samples, are shown in Figure 12. The presence of a phenolic matrix phase made a significant difference in energy absorption in PICA. The critical stress of crack initiation and growth exceeded 1000 kPa, for samples without notches and the ones with smaller (1.27 mm) notches. This magnitude is about twice the magnitude compared to tensile strength in FiberForm samples. However, the samples with longer (2.54 mm) notches failed at lower values averaging 700 KPa. This shows that, unlike FiberForm, the presence of longer notches did reduce the tensile strength in virgin PICA. This is again an important aspect to consider when attempting to model porous materials and providing the critical stress values in the presence of flaws.

The specimens showed nonlinear stress-strain relation early on starting at 0.3% strain. The strain-to-failure for these samples was in the range of 1.0% - 1.2% and tensile strength was in the range of 0.8 to 1.2 MPa, similar to the CM database values, obtained during the in-plane tension test for Orion project [13].

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Figure 13: Crack initiation in virgin PICA Specimen.

Figure 14: Matrix cracking and fiber bridging in virgin PICA

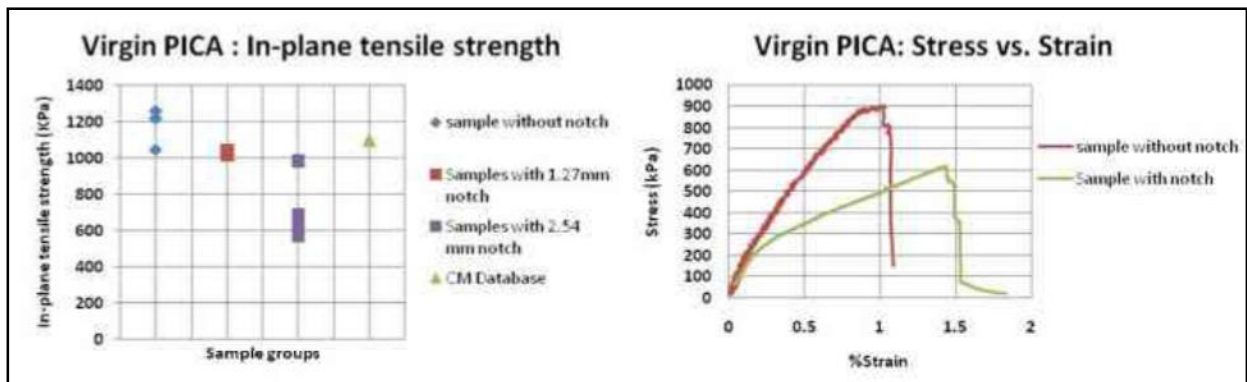**Figure 15: In-plane tensile strength and stress-strain data for virgin PICA specimens.**

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C. Charred PICA Tests

The charred PICA samples were prepared by two methods: charring the virgin material inside an inert furnace, and sectioning pieces off of the charred portion of arc-jet tested PICA articles. Several furnace charred PICA specimens with ~2.54 mm notch size were tested inside the electron microscope. The crack initiation and growth was rapid once the critical stress was achieved, showing very similar behavior as virgin PICA samples. Videos and micrographs were obtained for the notched specimens. The crack initiated in the porous matrix phase and the crack path followed the porous matrix. Carbon particle shedding in the porous matrix was also observed in some videos. Fiber pull-out and bridging phenomenon, similar to virgin PICA samples, were observed at some locations as shown in Figure16. Figure 17 shows the evidence of matrix cracking. Most specimens failed between 600 kPa - 900 kPa. The charred PICA samples made from arc-jet articles showed similar behavior and tensile strength as the furnace char. Again, based on test data from most of the samples, the introduction of a notch did not make significant difference in maximum tensile stress at which failure occurred. The stress-strain data and tensile strength for representative samples are shown in Figure 18. The maximum tensile stress achieved for these specimens was slightly higher than FiberForm samples but lower than virgin PICA. This suggests that fracture toughness of PICA ablator is driven by the extent of energy that can be absorbed by the porous matrix phase. The charred PICA specimens showed a similar non-linear stress-strain relation as FiberForm and virgin PICA samples. However, the strain-to-failure in charred PICA samples was lower than virgin PICA. To the best of our knowledge, to date no other tensile testing of charred PICA material has been conducted. This was the first test series where stress-strain plots and tensile strength data for the in-plane tension loading configuration were obtained.

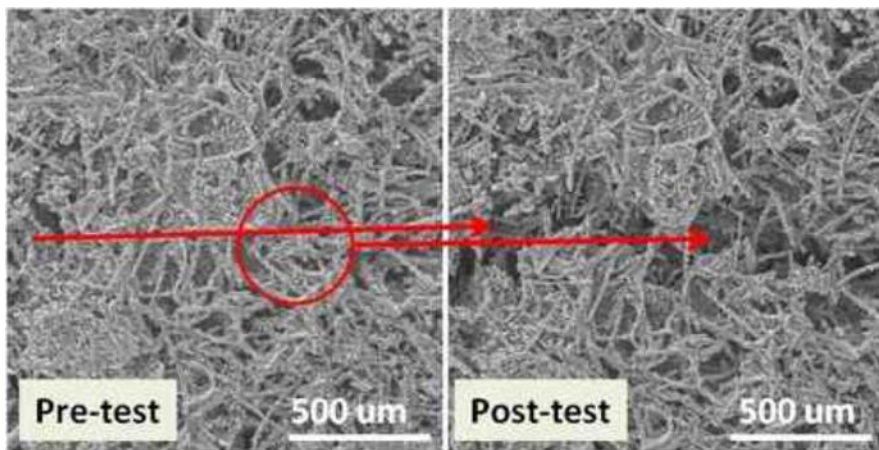**Figure 16: Crack initiation and growth in charred PICA coupons.**

Figure 17: Matrix cracking in charred PICA samples.

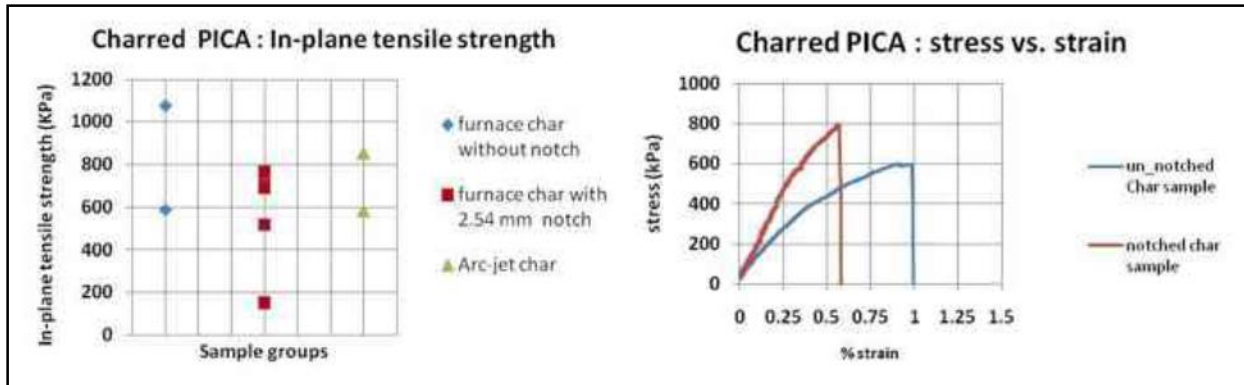American Institute of Aeronautics and Astronautics

Figure 18: In-plane tensile strength and stress–strain data for charred PICA specimens.

VI.   Conclusions

Successful fracture testing of FiberForm, virgin PICA and charred PICA inside an electron microscope was performed. This research proved that investigation of failure mechanisms for TPS materials can be successfully conducted at a microstructure scale. The tests provided valuable insights into failure mechanism of FiberForm and PICA materials. For notched samples, the crack initiated and grew at the notch tip and failure mechanisms in each of the materials was investigated at a microstructural scale by capturing videos of failure events and high magnification micrographs. FiberForm specimens fractured due to fiber pull-out from the carbonaceous binder wherever it was present in lower concentration. Occasional cracking of binder was also observed where it was sparse. In virgin and charred PICA, the fracture was governed by the cracking of the matrix phase. In PICA, the phenolic matrix phase plays an important role in absorbing the energy, and the fracture toughness of the material is significantly influenced by the toughness of the porous phenolic matrix. The stress-strain data were obtained simultaneously for each test. The data suggests that, for small flaws, the tensile strength is not affected, and the stress distribution inside the sample is governed by the material porosity. However, for larger flaws the critical failure stress values start to decrease. The in-plane tensile strength magnitude for FiberForm and virgin PICA was comparable to the values obtained during the CEV TPS ADP. The data suggests that this method can be very useful for obtaining reasonable estimates of the mechanical properties of charred ablators, including experimental TPS materials at TRL 1-2 stage where fabrication of large samples may not be possible. This research can also provide very valuable information for computational modeling of the fracture of porous materials and micromechanical modeling of TPS materials.

VII.   Acknowledgments

VIII.   References

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