

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 reentry which can threaten the structural integrity of the system. This paper discusses the development of a novel technique to understand the failure mechanisms inside the thermal protection material, Phenolic Impregnated Carbon Ablator (PICA). PICA has successfully flown on the Stardust spacecraft and was the TPS material chosen for the Mars Science Laboratory (MSL), that will fly in 2011. Although PICA has good thermal properties, structurally, it is a weak material. To thoroughly understand failure in PICA, experiments were performed using FiberForm®* (precursor of PICA), virgin and furnace-charred PICA. Several small samples were tested inside an electron microscope to investigate the failure mechanisms. Micrographs were obtained before and after the failure in order to study crack initiation and growth. Videos were obtained to capture failure mechanisms in real time. Stress-strain data was obtained simultaneously for all the samples with the help of a data acquisition system, integrated to the mechanical stages. 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 that could not survive the heating during re-entry¹. The study and analysis work involved with thermal protection materials is very complex. Several 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 of trajectory.

Phenolic Impregnated Carbon Ablator (PICA) was chosen for the present studies because it was the material used for the Stardust probe² and will be used in the heat shield for the Mars Science Lab (MSL)³ mission and Dragon spacecraft from Space-X. PICA was developed by scientists at NASA Ames⁴. As the name suggests, it is made by impregnation of phenolic resin within the carbon fiber preform named FiberForm, followed by a cure cycle at an elevated temperature. It could be viewed as a two phase material consisting of carbon fibers and a porous phenolic matrix as shown in Figure 1. The carbon fibers in the preform are oriented preferentially in the horizontal direction

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making it a transverse isotropic material with different material properties in through-the-thickness and in-plane directions. PICA is a low density ablator with extremely high porosity. In the presence of high heat flux, it pyrolyzes and forms a char layer. Although PICA has very good thermal properties, structurally, it is a weak material. Several studies are being performed to improve the structural properties of PICA without compromising the thermal properties or mass. The researchers at NASA Ames and Fiber Materials Incorporation (FMI) have been changing process parameters to alter the microstructure to improve mechanical properties⁵. It is important to understand mechanisms of crack initiation and propagation at a microstructural scale to provide guidance to optimize the microstructure. To accomplish this objective, fracture experiments were designed for PICA and FiberForm specimens that could be conducted inside the electron microscope. FiberForm was tested first to understand the failure mechanisms and tensile strength. In FiberForm, the carbon fibers are glued to each other in small groups by means of a 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 fiber 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 as shown in Figure 2. Some cross-linking that joins the fibers together and makes it a rigid preform also takes place during the processing. After testing Fiberform specimens, the tests were conducted on virgin PICA material at room temperature.

Ablative TPS materials are subjected to very high heat flux during atmospheric re-entry causing them to pyrolyze and char. Tests on charred PICA were performed to understand the affects of phase changes and temperature exposure on mechanical strength and failure mechanisms. Charred PICA samples were created by heating the specimens in a tube furnace to 1300⁰C in inert enviroment. All the specimens were heated until they were uniformly charred. The micrograph of a charred PICA specimen with a notch is shown in Figure 3. While all the organic material from the phenolic resin was evaporated, a thin carbonaceous matrix phase was still present between the carbon fibers. This phenomenon is also observed on the PICA char during re-entry of the Stardust probe⁶.

For each of these materials, initiation and propagation of cracks at a microstructure scale was captured. The stress strain data obtained during these experiments will assist in providing the material properties input for thermal-structural finite element modeling.

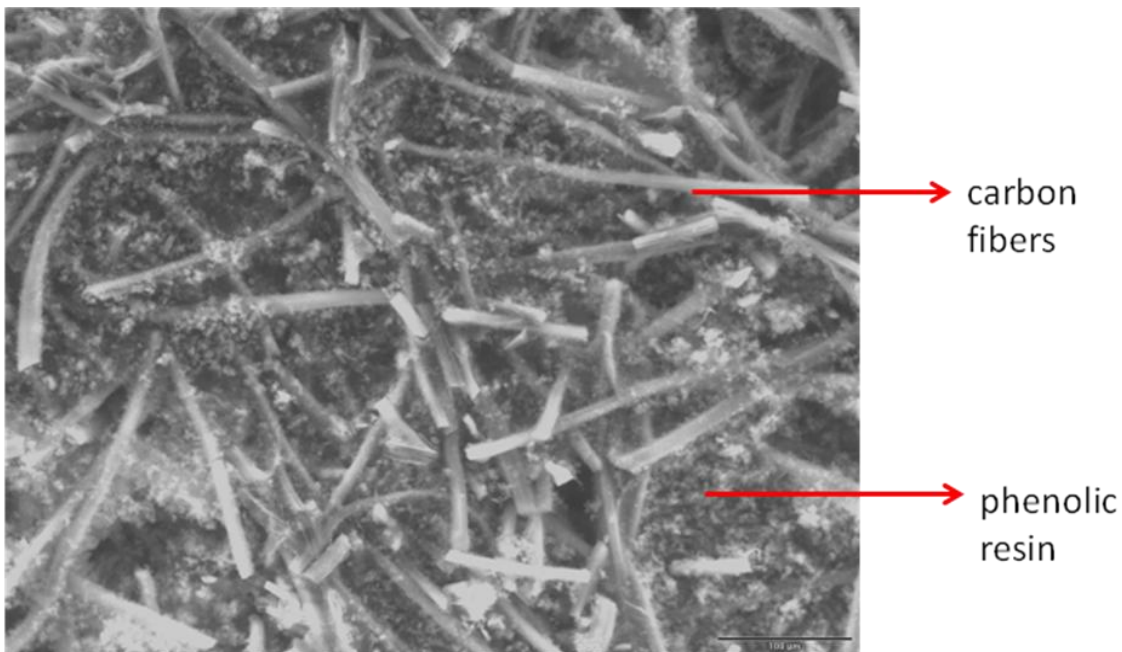


Figure 1: PICA microstructure (substitute a better micrograph).

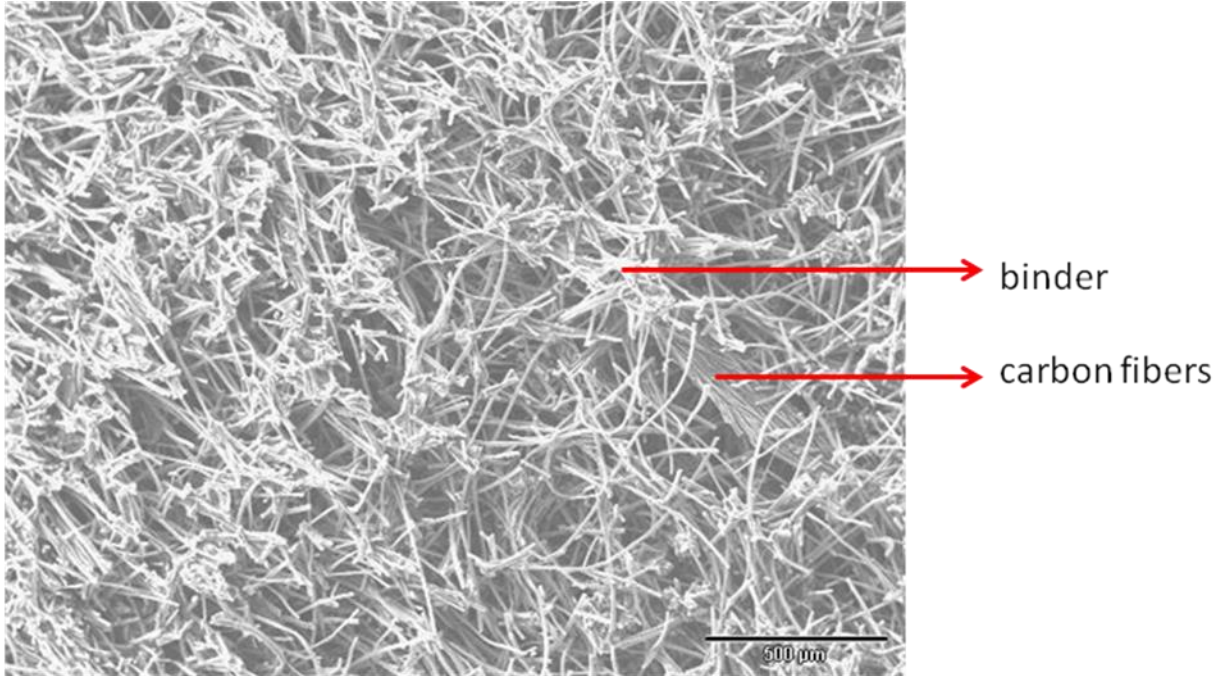


Figure 2: FiberForm microstructure (will substitute a higher magnification micrograph).

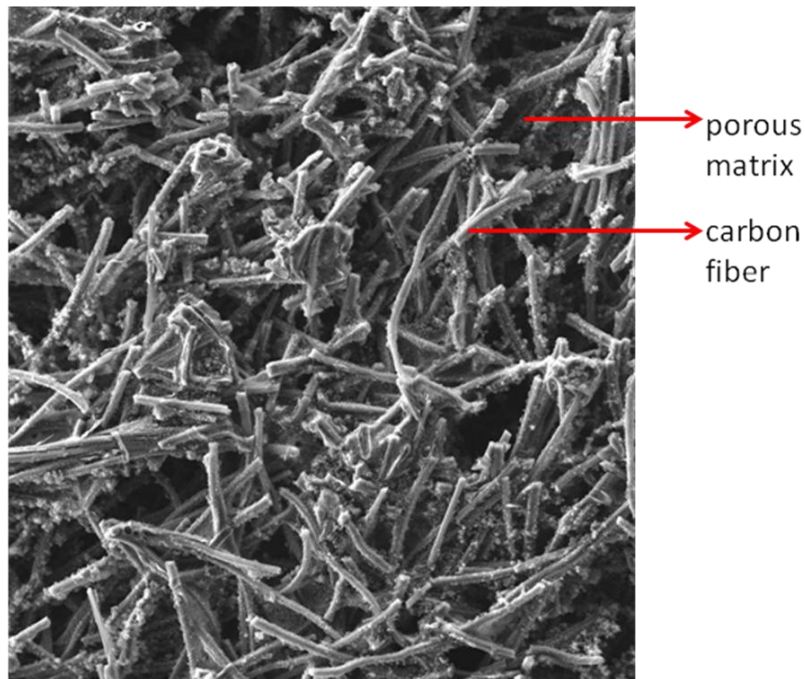


Figure3: Charred PICA microstructure

II. Instrumentation

The experiments were performed inside a Philips XL-30 electron microscope unit from FEI. A miniature custom designed mechanical stage was mounted inside the microscope chamber as shown in Figure 4. A data acquisition

system was also added to the system 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, Figure 5. There was a strain transducer mounted on the stage that provided the displacement measurements. A heating unit could be mounted on the stage to perform mechanical tests at elevated temperatures ranging from -40°C – 1100°C . The sample sizes could vary 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.

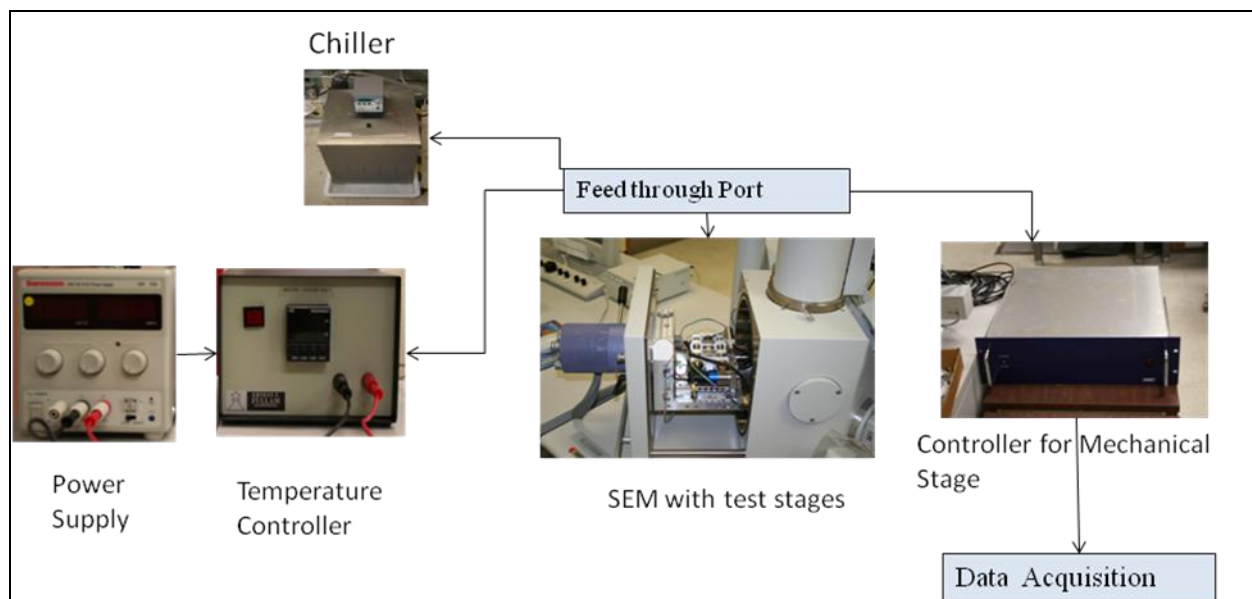


Figure 4: Experiment set-up for in-situ SEM fracture experiments

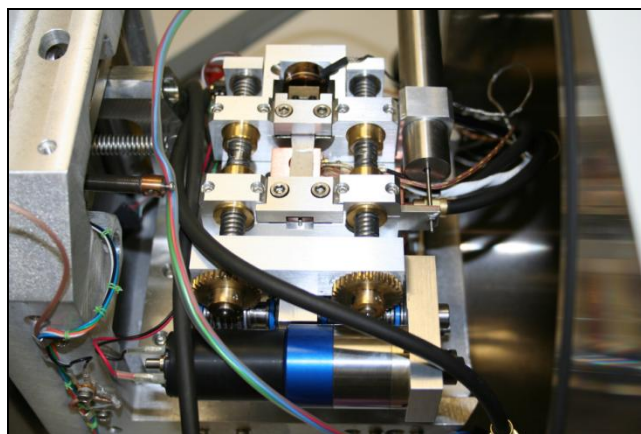


Figure 5: Mechanical sub-stage

III. 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 on samples at the midline, using a micro scribe tool. One of the notched PICA samples is shown in Figure 7. Specimens were created with two different notch lengths of 1.15 mm and 2.3 mm. The notch tip radius in most specimens was approximately 100 μm . These dimensions were sufficient to initiate crack and view the failure mechanisms at a microstructural scale. Thin aluminum tabs were glued to the ends of all the coupons with help of transfer coated RTV (room temperature vulcanized) adhesive. This was required to avoid any local damage, slipping and premature failure of specimens near the grips.

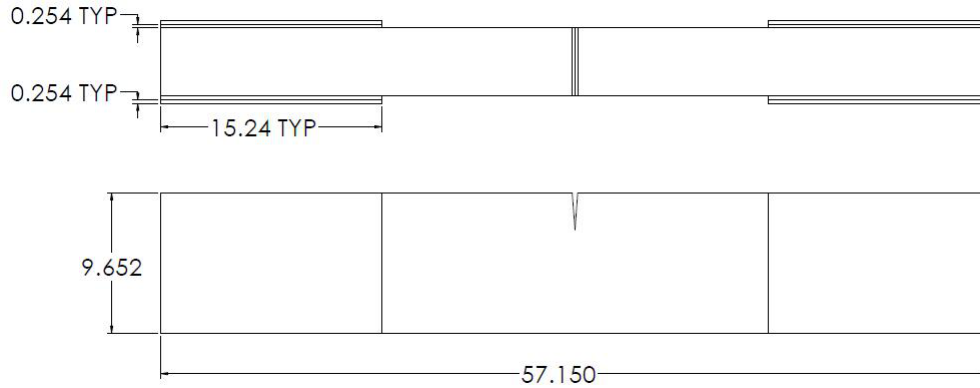


Figure 6: Specimen geometry (dimensions in mm).

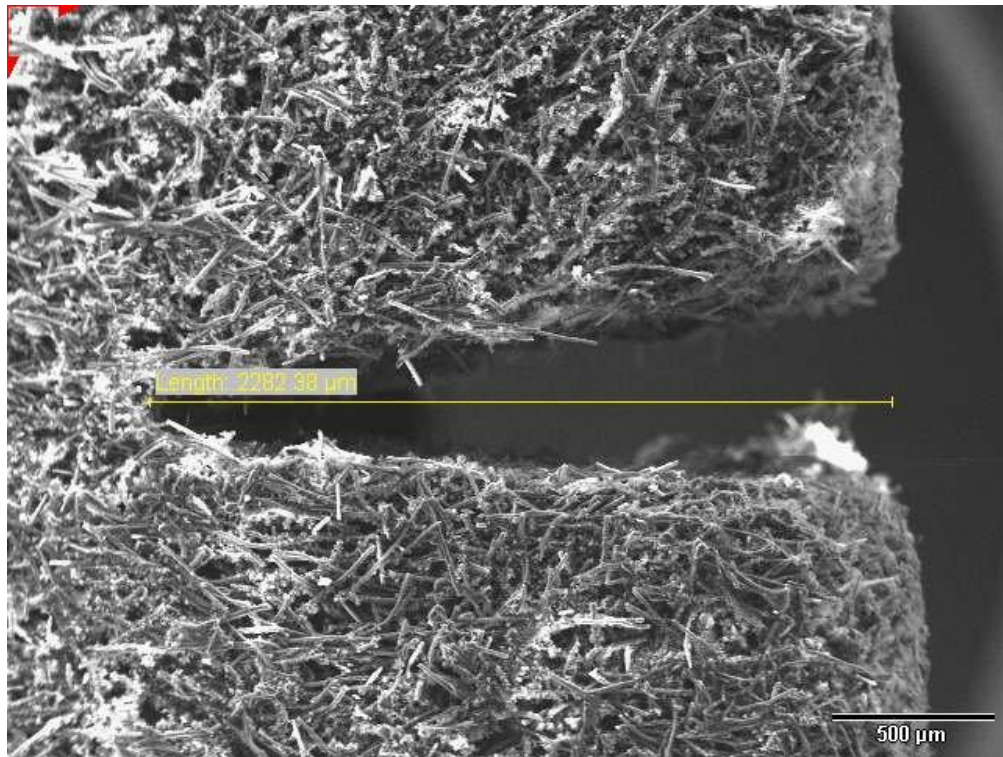


Figure 7: Micrograph of PICA coupon with a notch.

IV. Test Results and Analysis

In-plane tension tests were performed at room temperature under high vacuum of 3.0×10^{-4} mBar. All the samples were pulled inside the SEM chamber. 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 magnification 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 flaws in stress-strain relations. For some materials like charred PICA there is no tension test data available. The pull tests helped to obtain the tensile strength and toughness of charred PICA materials. The in-plane young's modulus and tensile strength data for FiberForm and virgin PICA obtained during the tests were compared with Crew Exploration Vehicle (CEV) material properties database values to validate the tests and establish accuracy⁷.

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 specimen 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 a micrograph of fiber separation near the binder phase. Fiber cracking was not observed in any of the specimens. The stress-strain data for representative un-notched and notched FiberForm coupons are shown in Figure 7. All the specimens fractured in the range of 500-600 kPa stress magnitude and a difference in tensile strength due to the presence of notches was not observed. The data also suggested nonlinear stress-strain behavior from the very beginning. For most specimens, the strain-to-failure was between 0.6%-1.0%. More experiments are needed to investigate whether the presence of notches changed the strain-to-failure magnitude. The strength data is comparable to the data obtained on FiberForm for the Orion program⁷.

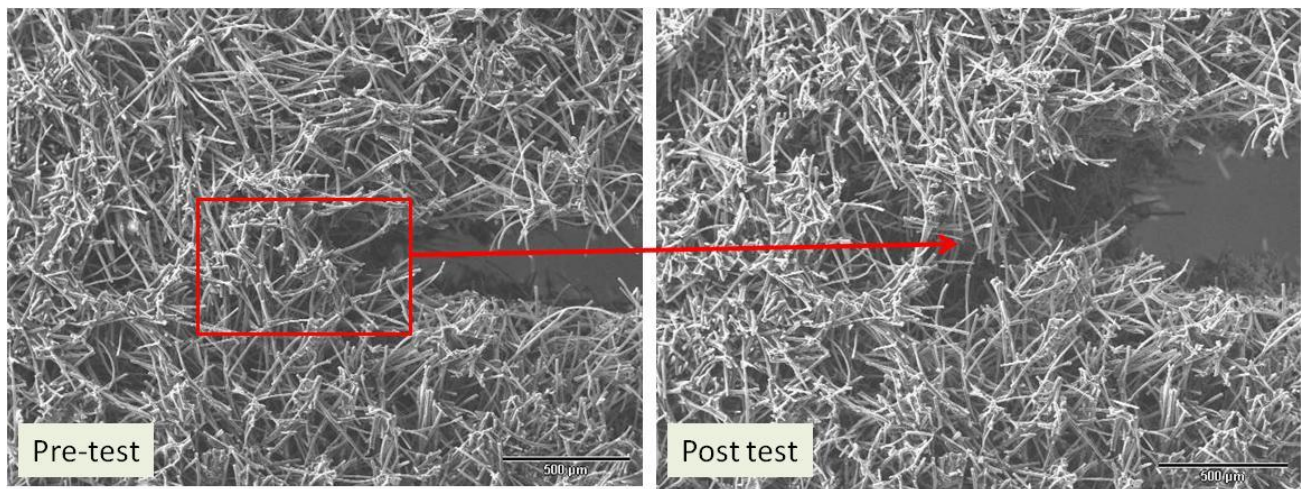


Figure 8: Crack initiation in FiberForm.

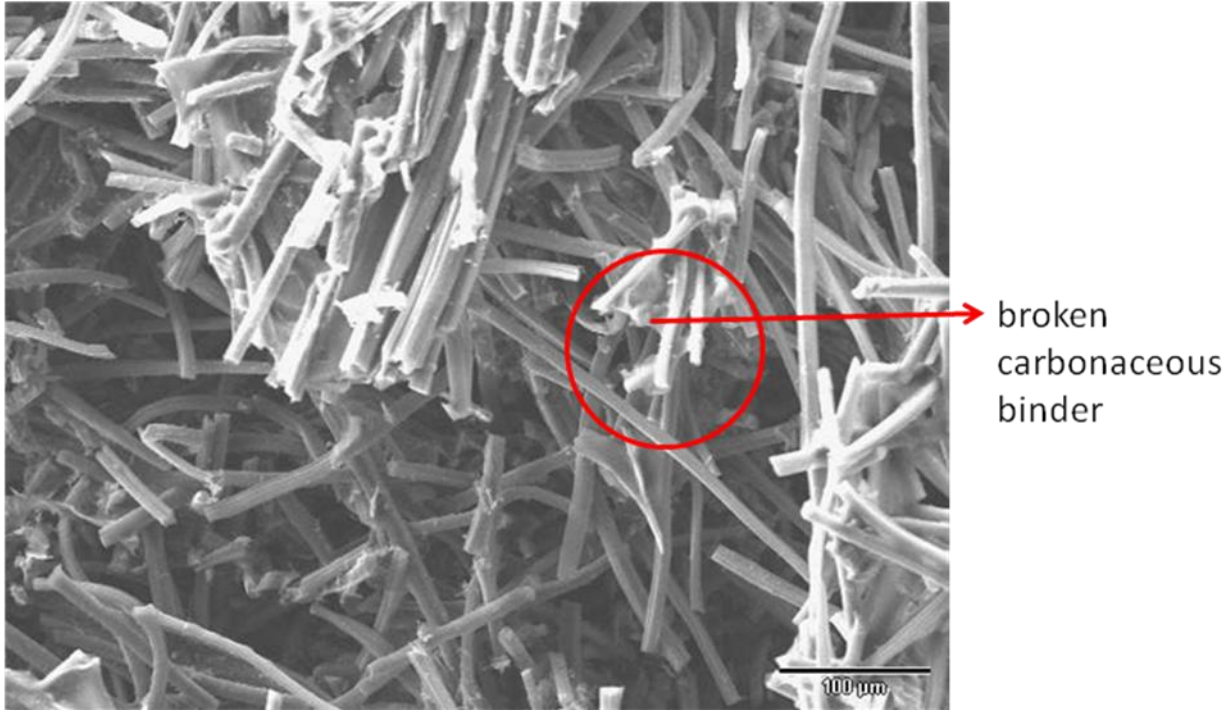


Figure 9: Fiber separation near the binder.

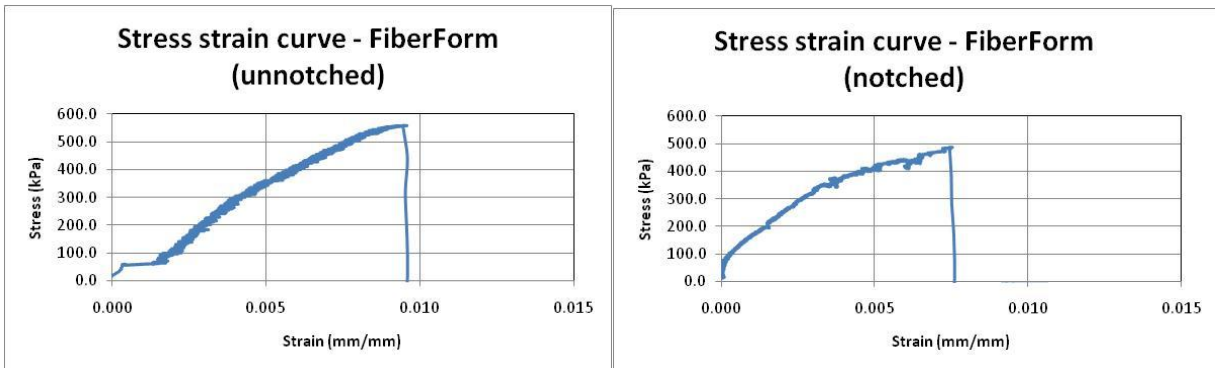


Figure10: Stress-strain data for FiberForm specimens.

B. Virgin PICA Fracture Tests

Fracture tests were performed on both notched and un-notched PICA samples. The dimensions were kept constants across the samples to obtain consistent results. Specimens were fabricated with two different notch sizes, 1.15mm and 2.25 mm, to investigate the effects of flaw size on strength and mechanical behavior.

Similar to FiberForm, PICA samples 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 11. 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 Figure 12. Stress-strain data was obtained for all the specimens. A representative stress-strain plot for un-notched and notched PICA samples is shown in Figure 12. The presence of a phenolic matrix phase made a significant difference in energy absorption. The critical stress of crack initiation and growth exceeded 1000 kPa, about twice the magnitude compared to tensile strength in FiberForm specimens. Therefore, the microstructure of a matrix phase plays a critical role in enhancing the tensile strength and fracture toughness of PICA. With limited testing of 8 samples no difference was observed in the tensile strength of specimens for samples with notches compared to samples without notches. More testing is required to investigate the critical flaw size that would significantly lower the tensile strength of virgin PICA material. This aspect will be important to consider for finite element modeling and will be discussed in detail in Section V. 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 data obtained during the in-plane tension test for Orion project⁷.

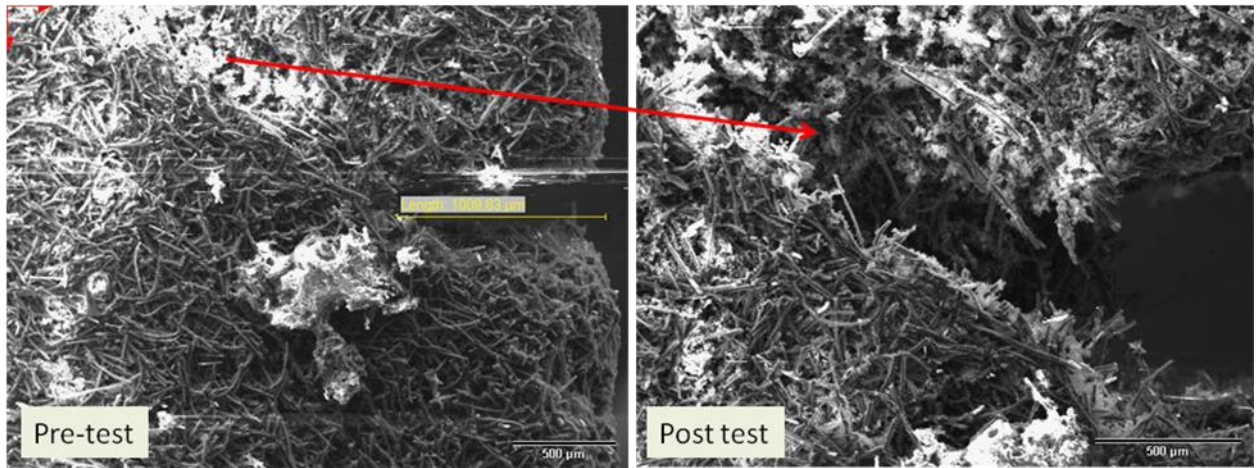


Figure 11: Crack initiation in virgin PICA Specimen.

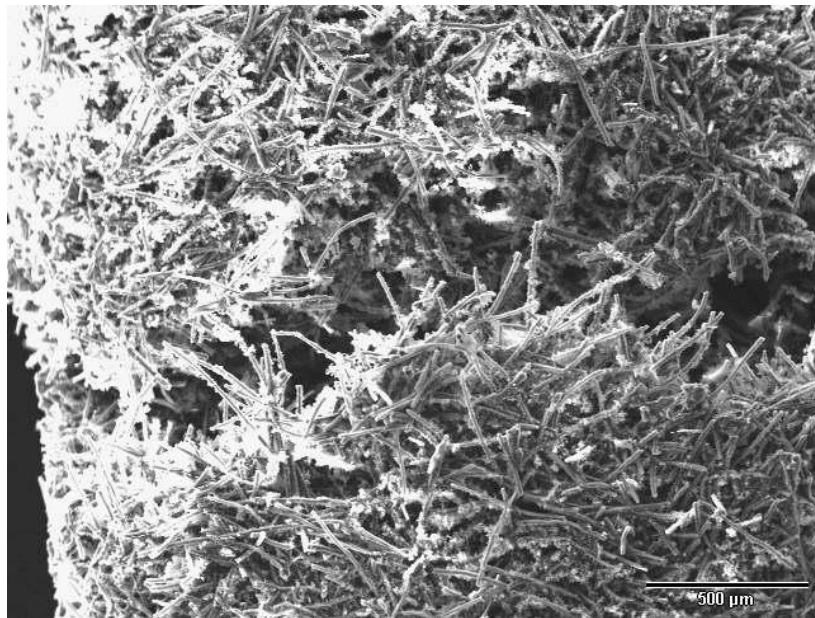


Figure 12: Matrix cracking and fiber bridging in virgin PICA

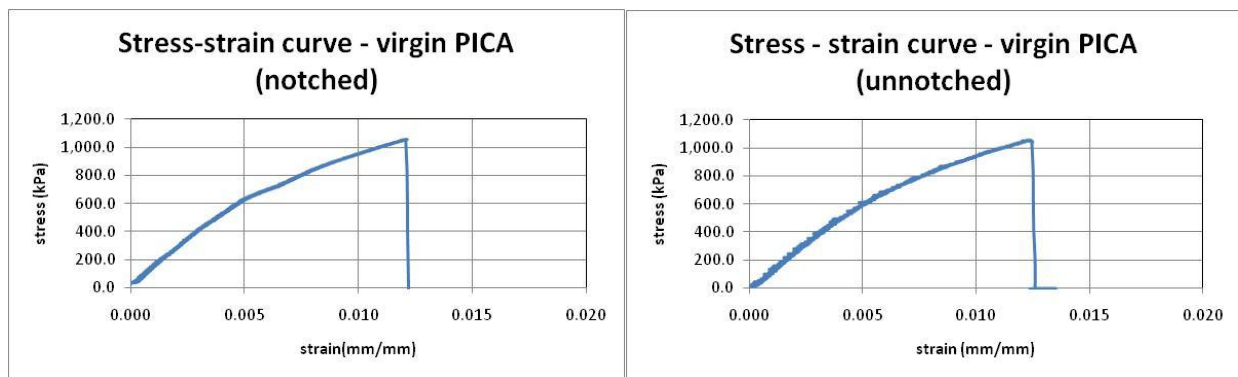


Figure 13: Stress-strain data for virgin PICA specimens.

C. Charred PICA Tests

Several specimens with ~2.3 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 Figure 14. The stress-strain data and tensile strength for representative samples are shown in Figure 15. Most specimens failed between 600 kPa - 900 kPa. Again, based on test data from 8 samples, the introduction of a notch did not make any difference in maximum tensile stress at which failure occurred. The maximum tensile stress achieved for these specimens was slightly higher than FiberForm samples but significantly 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 date, based on our knowledge; 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.

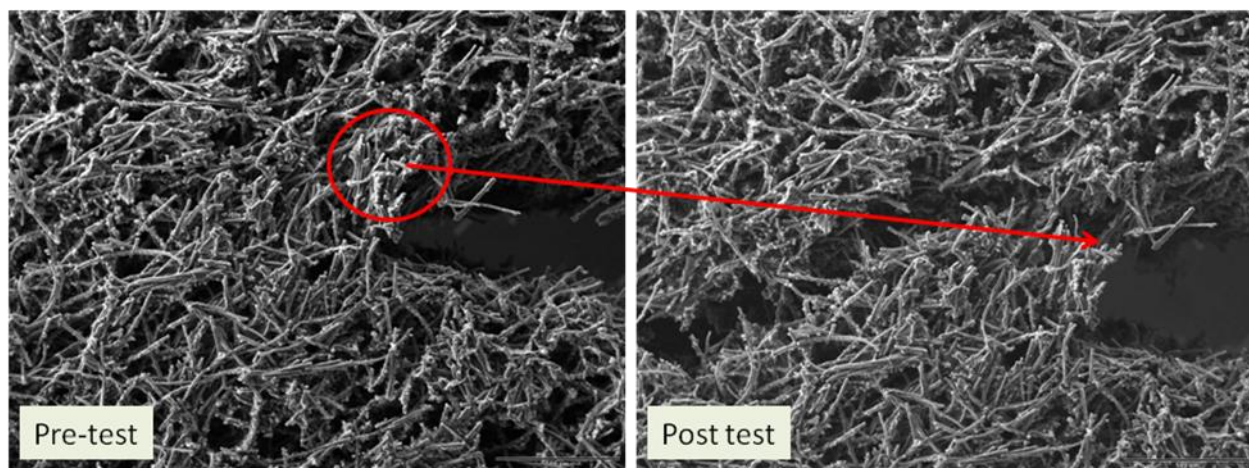


Figure 14: Crack initiation and growth in charred PICA coupons.

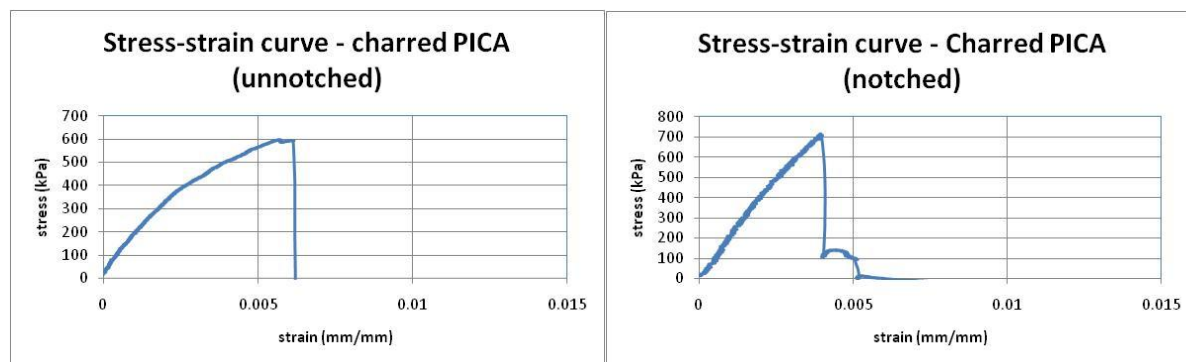


Figure 15: Stress – strain data for charred PICA specimens.

V. Fracture Toughness Calculation and Modeling

Calculation of fracture toughness for PICA is non-trivial as it is a transverse isotropic composite with a porous matrix phase. Finite element analysis of the mechanical loading and changes in structural response in the presence of flaws in porous ablators is also very important. This work is in progress and this section will be discussed in the final paper.

VI. Conclusions

Successful fracture testing of FiberForm, virgin PICA and charred PICA inside the electron microscope was performed. 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. 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 determined by the toughness of the porous phenolic matrix. The stress-strain data was 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. The in-plane tensile strength magnitude for virgin PICA was comparable to the values obtained during the Orion program.

VII. Acknowledgments

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VIII. References

¹Columbia Crew Survival Investigation Report, NASA SP-2008-565, 2008.

²Willcockson, W.H. "Stardust Sample Return Capsule Design Experience," *Journal of Spacecraft and Rockets*, Vol. 36, No. 3, 1999, pp. 470-474.

³Lockwood, M.K., “Introduction: Mars Science Laboratory: The next generation of Mars Landers,” *Journal of Spacecraft and Rockets*, Vol. 43, No. 2, 2006, pp. 257.

⁴Tran, H., Johnson, C, Rasky, D., Hui, F., Chen, Y.-K., and Hsu, M., “Phenolic Impregnated Carbon Ablators (PICA) for Discovery Class Missions,” AIAA Paper 96-1911, June 1996.

⁵Fan W., et. al. “Strengthening PICA with Functionalized Carbon Nanotubes”, NASA TM-2010-216388, 2010

⁶M. Stackpoole M., Sepka S., Cozmuta I., and Kontinos D. “Post-flight evaluation of stardust sample return capsule forebody heatshield material” , AIAA-2008-1202, 46th AIAA Aerospace Sciences Meeting and Exhibit, , January 2008.

⁷Feldman J., Alunni A., Stackpoole M., “Thermal and Mechanical Property Testing Orion Heat Shield Candidates”, 34th Annual Conference on Composites, Materials, and Structures, January 25-28, 2010 Cocoa Beach / Cape Canaveral, Florida.