Dynamic Mechanical Analysis (DMA) to Help Characterize Vespel SP-211 Polyimide Material for Use as a 750°F Valve Seal on the Ares I Upper Stage J-2X Engine

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August 6, 2013

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- DuPont™ Vespel® SP-211 polyimide was selected as the top candidate seal material for use in the Oxidizer Turbine Bypass Valve (OTBV) in the J-2X Upper Stage engine of NASA's Ares I manned flight vehicle.

  - The program for the Ares I vehicle was cancelled, but the J-2X engine was chosen for continued use in development of NASA's Space Launch System (SLS), a heavy-lift launch vehicle capable of leaving Earth orbit and going into deep space. The J-2X was built by Pratt & Whitney Rocketdyne (PWR).

  - The Vespel SP-211 material in the OTBV could be exposed to multiple temperature cycles up to 750°F for ≈10 minutes at a time during engine operation. DuPont determined the upper limit continuous use temperature of SP-211 as 500°F, with allowable excursions to 900°F.

  - Vespel SP-211 contains 15 weight % graphite powder and 10 weight % PTFE polymer.

  - Dynamic Mechanical Analysis (DMA) was the primary of several experimental techniques used to characterize Vespel SP-211 to help prove its worthiness for use on the OTBV of the J-2X engine.

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Fig. 1. Steps in sample preparation for various tests on Vespel SP-211.

Left—Broken tensile specimen from Pratt & Whitney Rocketdyne (PWR) was machined down the middle with a low speed circular saw to make two rectangular samples. The longer of the two samples was tested in the DMA by three-point bending.

Middle—The remainder of the tensile specimen was machined into 25-30 small cubic-to-rectangular pieces with a low speed circular saw.

Right—The small pieces (middle) were ground into a powder with a freezer/mill. Powdered samples were used for porosity, DSC, TGA testing and IR spectroscopy.

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Table 1. Tensile specimens of Vespel SP-211 tested at Pratt & Whitney Rocketdyne (PWR) and NASA/Marshall Space Flight Center (MSFC).

70°F Tensile Tests		
PWR sample I.D.	PWR Sample Description	Tested at MSFC
ARC-4, -5, -6	As-machined control	ARC-4, ARC-5
AR2X-4, -5, -6	As-machined + 2 cycles thermal shock	None
AR5X-4, -5, -6	As-machined + 5 cycles thermal shock	None
AR10X-4, -5, -6	As-machined + 10 cycles thermal shock	AR10X-4
CC-1, CC-2	Thermal conditioned control	CC-1
C2X-1, C2X-2	Thermal condition + 2 cycles thermal shock	None
C5X-1, C5X-2	Thermal condition + 5 cycles thermal shock	C5X-1
750°F Tensile Tests		
ARC-7, -8, -9	As-machined control	ARC-7, ARC-8
AR2X-7, -8, -9	As-machined + 2 cycles thermal shock	AR2X-7
AR5X-7, -8, -9	As-machined + 5 cycles thermal shock	AR5X-7
AR10X-7, -8, -9	As-machined + 10 cycles thermal shock	AR10X-7, AR10X-8
CC-3, CC-4	Thermal conditioned control	CC-3
C2X-3, C2X-4	Thermal condition + 2 cycles thermal shock	None
C5X-3, C5X-4	Thermal condition + 5 cycles thermal shock	C5X-3, C5X-4

- One thermal conditioning cycle: Heat (anneal) material at a slow heating rate to 399°C (750°F) and hold for a specified time. Turn off furnace and do not open until temperature is ≤ 100°F.
- One thermal shock cycle: Immediately expose material to 750°F and soak at that temperature for 10 min. Remove the material and cool to ambient temperature. Repeat procedure until desired total of thermal shock cycles are performed.

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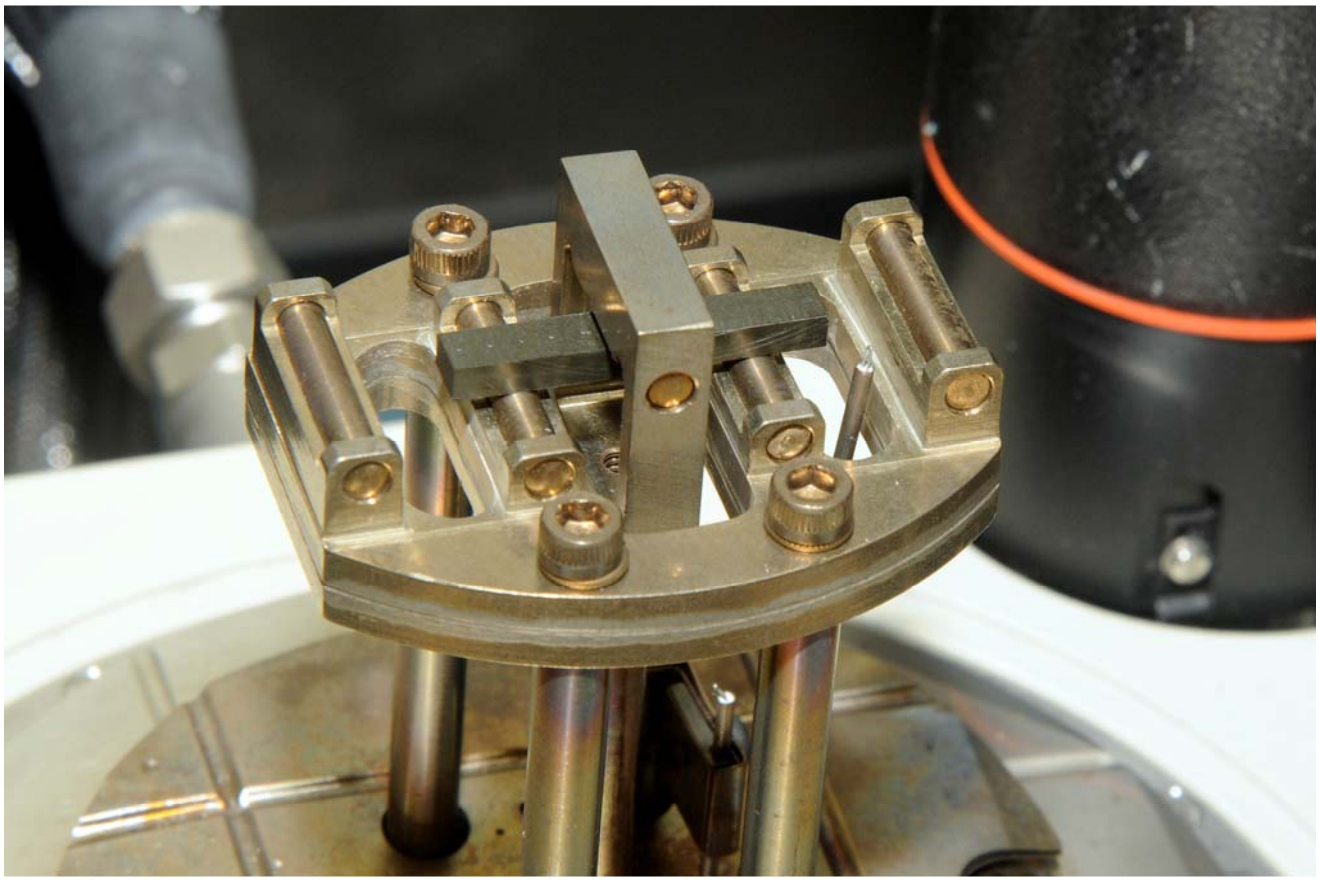
Fig. 2. Vespel SP-211 sample machined from broken tensile specimen and mounted in the DMA three-point bend clamp for testing. The DMA used was the 2980 model made by TA Instruments.



- Used 20 mm length three-point bend clamp.
- Amplitude (displacement) of 30 μm.
- Frequency of 1 Hz.
- Flowing air test environment at ≈ 65 psi.
- For each sample, 10 heat-cool-heat cycles between 20 and 400°C (752°F) at 4°C/min., with a 10 min. hold at 400°C for each heating scan.
- Initial static force of 0.1 N for each sample test.
- Average sample thickness of 3.19 mm, ➔ L/T = 6.27. This thickness, along with no measurable Tg, prevented sample sag.

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Fig. 3. DMA plot of storage modulus and temperature vs. time for 10 heating and cooling scans on a sample of Vespel SP-211 (ARC-4, as-machined control tensile tested at 70°F). There was a 10-min. hold at 400°C at the end of each heating scan.

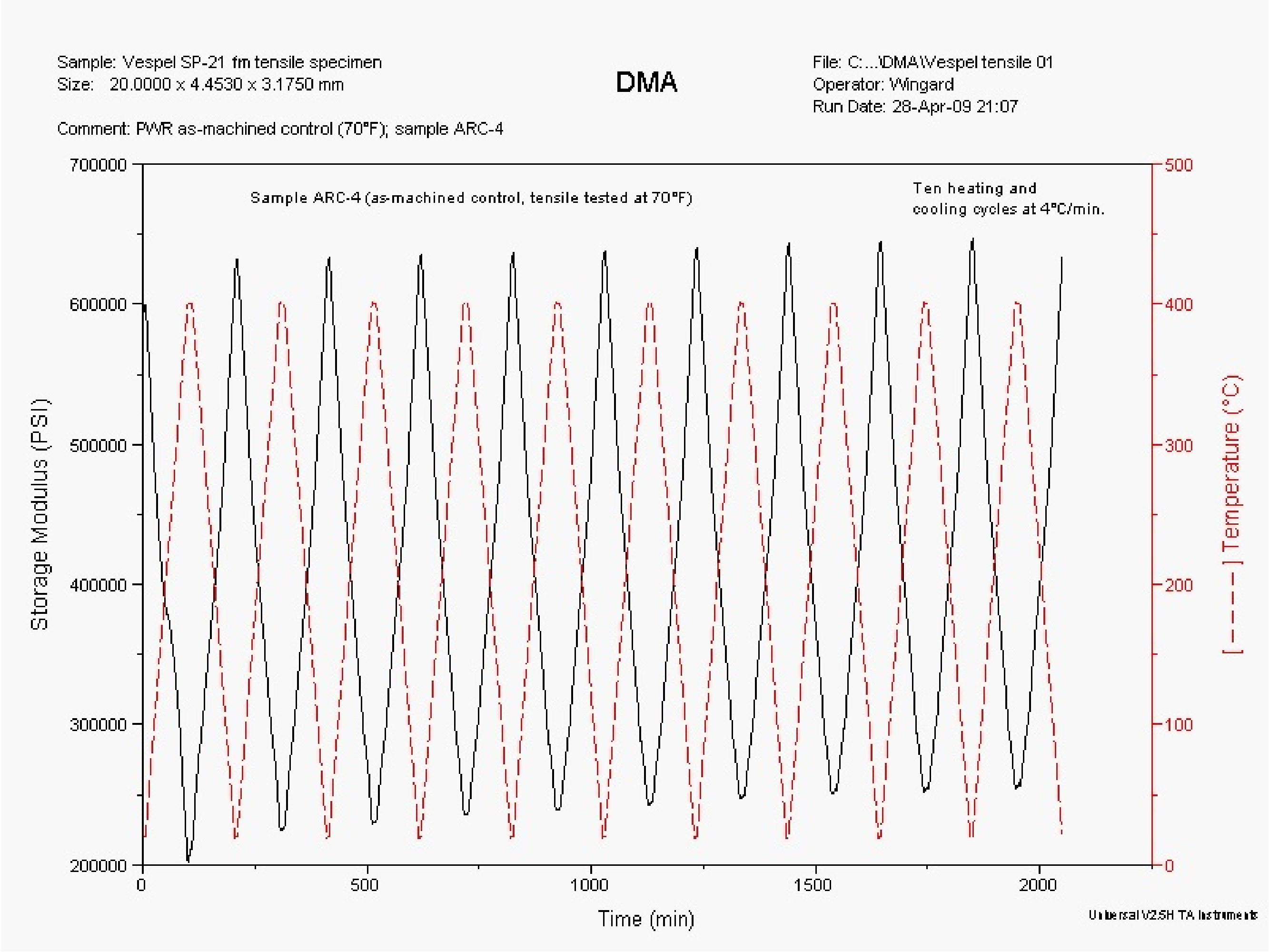

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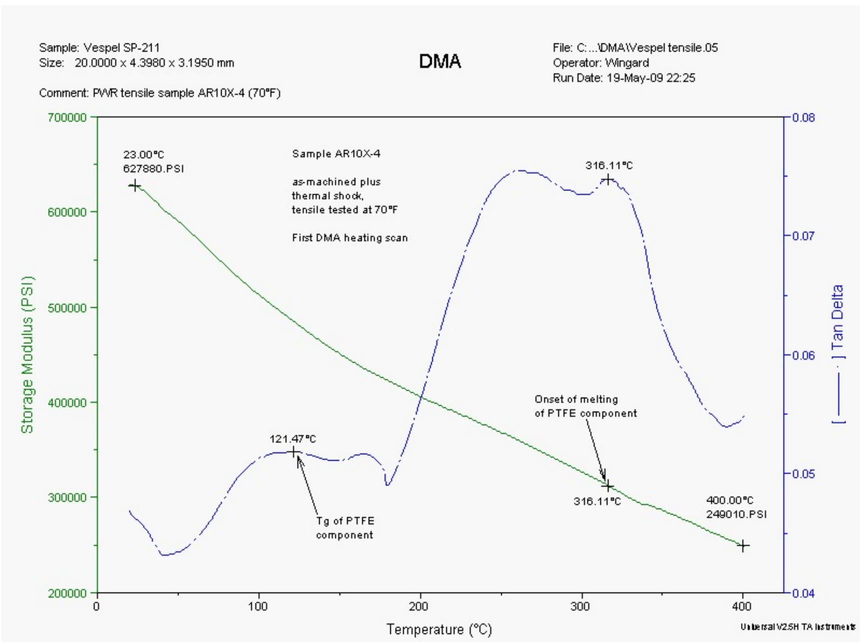
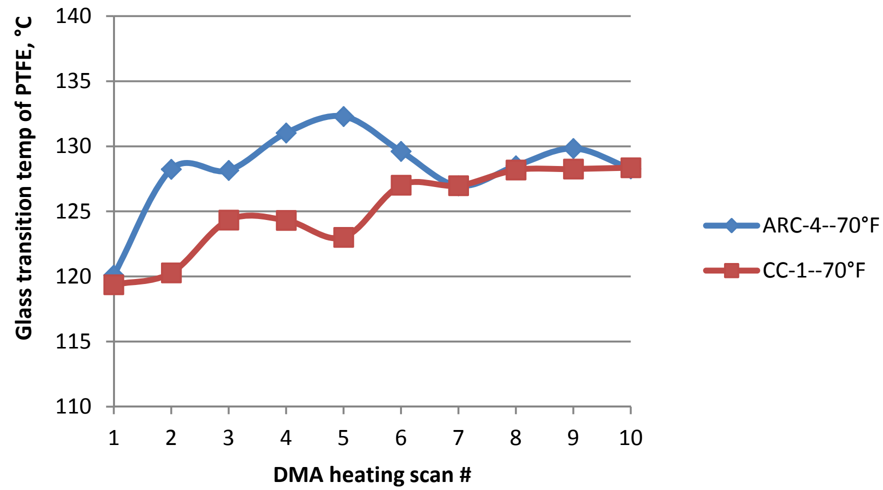
Fig. 4. ***Left:*** DMA plot of storage modulus and tan delta vs. temperature for a Vespel SP-211 sample (AR10X-4, as-machined + 10 cycles of 750°F thermal shock). This is a plot for the first heating scan only. Tan delta peaks at 121°C and 316°C are for the PTFE component in SP-211: alpha glass transition temperature and melting temperature, respectively.





Right: For the PTFE component in Vespel SP-211, there was some variation of Tg and Tm (onset) with # of DMA heating scans. Thermal conditioning (CC) appeared to slightly lower Tg and Tm (onset) compared to as-machined (ARC) samples.

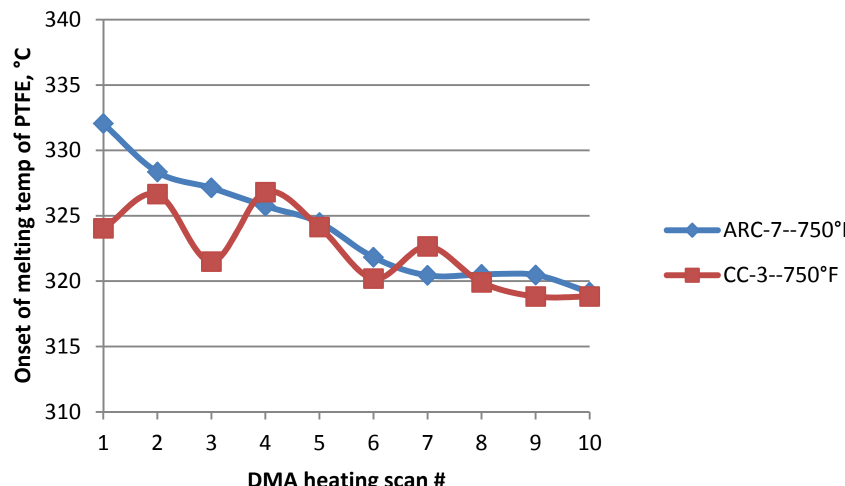


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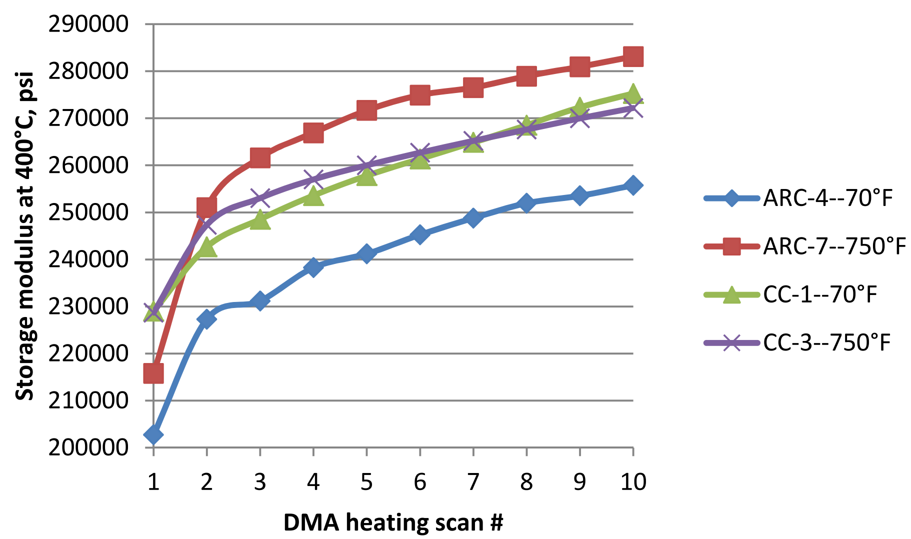
Fig. 5. DMA plot of storage modulus at 400°C vs. heating scan # for as-machined controls (ARC-4, -7) and thermally conditioned controls (CC-1, -3) that were tensile tested at 70°F and 750°F.



- This type of plot was made for all Vespel SP-211 samples tested by DMA. A good portion of the increase in storage modulus for each sample occurred between heating scan #'s 1 and 2.

- Thermally conditioned controls tensile tested at 70 and 750°F showed a substantial increase in modulus over an as-machined control tensile tested at 70°F.

- An as-machined control tensile tested at 750°F showed the highest increase in modulus vs. heating scan # in Fig. 5.

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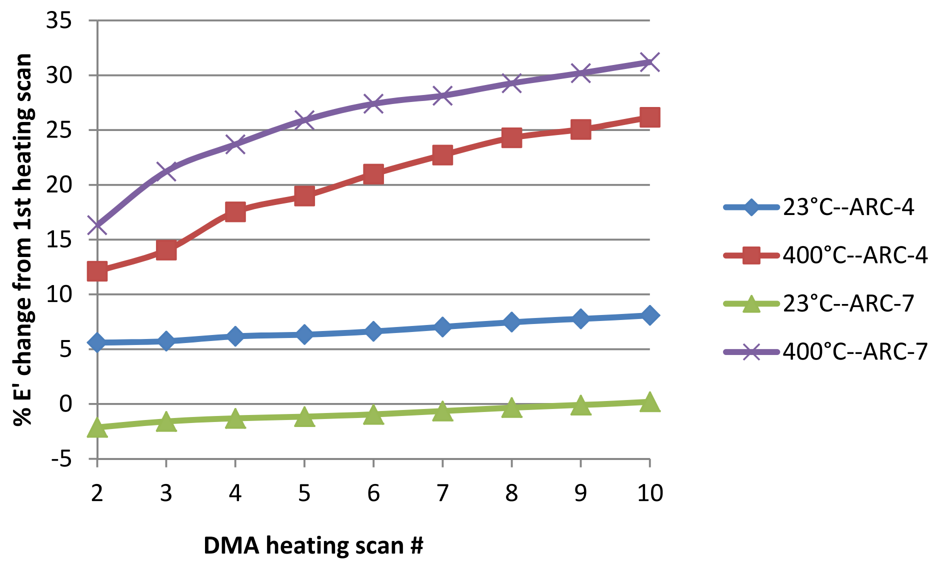
Fig. 6. ***Left:*** Percent change in DMA storage modulus (based on 1st heating scan) vs. heating scan # at 23°C and 400°C for as-machined control samples: ARC-4 (tensile tested at 70°F) and ARC-7 (tensile tested at 750°F).



Prior tensile testing history of sample used in DMA	***# of DMA heating scan (2 to 10) for E' > 20% increase at 400°C***
As-machined control, test at 750°F	3
As-machined control, test at 70°F	6
As-machined + 5 thermal shock cycles, test at 750°F	8
As-machined + 2 thermal shock cycles, test at 750°F	9
Thermally conditioned control, test at 70°F	10
Thermally conditioned + 5 thermal shock cycles, test at 70°F	10

- ***Right:*** The table shown is a summary of data of the type shown in the plot in Fig. 6.
  - For DMA heating scan #'s 2 to 10 for each Vespel sample, *an increase in E' >20% at 400°C was considered undesirable*.
  - The last two rows in the table indicate that thermal conditioning/annealing of a Vespel SP-211 part before use would give it better thermal stability during repeated heat cycling up to 750°F. An as-machined part would not have such thermal stability.

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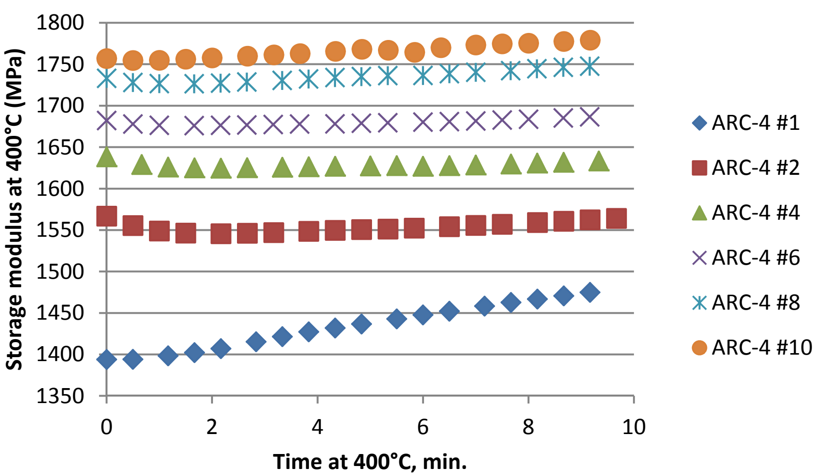
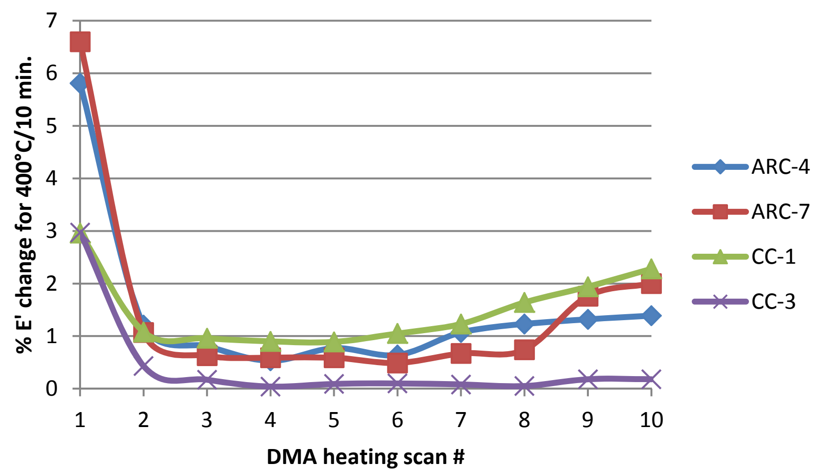
Fig. 7. ***Left:*** DMA storage modulus at 400°C vs. time at 400°C (0-10 min.) for sample ARC-4 (as-machined control tensile tested at 70°F). Modulus vs. time curves are shown for DMA heating scan #'s 1, 2, 4, 6, 8 and 10.

Right: Percent change in DMA storage modulus (400°C/10 min.) vs. heating scan # for Vespel SP-211 control samples: as machined (ARC-4, -7 tensile tested at 70, 750°F) and thermally conditioned (CC-1, -3 tensile tested at 70, 750°F).





- % change in storage modulus E' at 400°C was a concern, as was % change in E' at 400°C during a 10-min. hold.
- Unlike % change in E' at 400°C vs. # of heating scans, *% change in E' at 400°C during a 10-min. hold was not more than +6.6% for any Vespel SP-211 sample.*
- The thermally conditioned control tensile tested at 750°F (CC-3) showed little or no change in E' at 400°C/10 min. for heating scans 2-10, *indicating that such annealing plus some 750°F exposure may enhance thermal stability of SP-211*.

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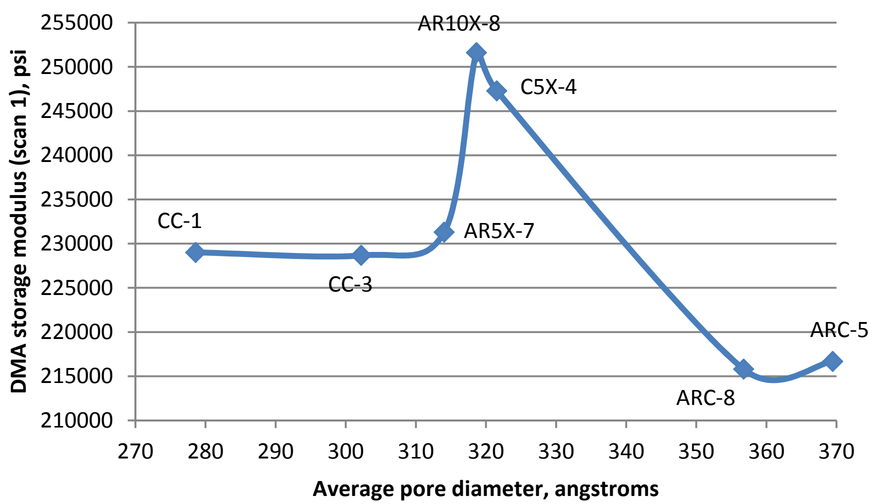
Fig. 8. DMA storage modulus (from 1st heating scan) vs. porosity (avg. pore diameter of intermediate-to-larger pores) for several powdered samples of Vespel SP-211.



Sample Legend	
CC-1	Thermally conditioned control, tensile test at 70°F
CC-3	Thermally conditioned control, tensile test at 750°F
AR5X-7	As-machined + 5 cycles thermal shock, tensile test at 750°F
AR10X-8	As-machined + 10 cycles thermal shock, tensile test at 750°F
C5X-4	Thermally conditioned + 5 cycles thermal shock, tensile test at 750°F
ARC-8	As-machined control, tensile test at 750°F
ARC-5	As-machined control, tensile test at 70°F

- Average pore diameter ranged from ≈ 280-370 Å. For geologic rock material, this is intermediate or "meso" porosity.
- Quality porosity data could not be obtained until each SP-211 sample was ground into a powder with a freezer/mill.
- Fig. 8 shows that as-machined controls had the highest porosity, and thermally conditioned controls had the lowest porosity (another advantage of annealing). Samples with 5-10 cycles of thermal shock were about in the middle range of all the measured porosity values for SP-211 material. These mid-range porosities correlated with the highest values of E'.

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- Summary and Conclusions

  - DuPont Vespel® SP parts and shapes yield a material with ≈25-50% crystallinity. Yet, such a material is not a true thermoplastic (no observable melting point) and is closer to a thermoset material.

  - Vespel SP-211 material was chosen for a hot gas valve in a NASA upper stage rocket engine, and the SP-211 could be exposed to multiple cycles up to 750°F for ≈10 min. at a time during engine operation. Vespel SP-211 contains 15 weight % graphite powder and 10 weight% PTFE polymer.

  - Ten (10) DMA heat-cool-heat cycles were performed on molded samples of Vespel SP-211. These samples had previous thermal histories such as 2, 5 and 10 thermal shock cycles at 750°F.

  - During the 10 controlled heating scans (4°C/min.) for each SP-211 sample, an increase in DMA storage modulus E' > 20% at 400°C (752°F) was considered undesirable. Such a significant increase in modulus could lead to increases in cross-link density and brittleness for a thermoset-like material such as SP-211.

  - For SP-211 samples with a prior history of thermal condtioning/annealing, DMA data indicated these samples had much greater resistance to E' > 20% at 400°C than as-machined samples.

  - Samples of SP-211 with 5-10 previous thermal shock cycles at 750°F had mid-range porosities for all powdered samples measured. These mid-range porosities correlated with the highest values of storage modulus determined by DMA on molded samples.