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

Doug Wingard[1]
[1] NASA/Marshall Space Flight Center, Mail Code EM10, Marshall Space Flight Center, Alabama 35812, doug.wingard@nasa.gov

ABSTRACT

DuPont™ Vespel® SP-211 polyimide was selected as the top candidate seal material for use in the Oxidizer Turbine Bypass Valve (OTBV) on NASA's Ares I Upper Stage J-2X engine. In the OTBV, the seal material would get exposed to temperatures up to 750°F for ~10 minutes at a time. Although the J-2X engine is not reusable, the valve material could be exposed to multiple temperature cycles up to 750°F during engine operation. The Constellation Program that included the Ares I rocket was eventually cancelled, but the J-2X engine was chosen for continued use for development of NASA's Space Launch System (SLS). The SLS is a heavy-lift launch vehicle that will have capability of taking astronauts and hardware to the Moon, Mars and asteroids. Dynamic mechanical analysis (DMA) was one of several test techniques used to characterize Vespel SP-211 to help prove its worthiness for use on the OTBV of the J-2X engine.

INTRODUCTION

Vespel SP-211 contains 15 weight percent graphite powder and 10 weight percent PTFE Teflon®. DuPont has determined the upper limit continuous use temperature of Vespel SP-211 to be 500°F, with allowable excursions to 900°F [1]. Compression hysteresis data was obtained on specimens of Vespel SP-211 from a mechanical testing machine at the NASA Marshall Space Flight Center (MSFC) in Alabama. Such compression testing at room temperature and 750°F yielded satisfactory results, but such data does not reveal what might happen to the SP-211 material at a molecular level with repeated elevated temperature exposure beyond its normal 500°F limit.

As a basis for molecular characterization testing at MSFC, portions of broken mechanical property tensile specimens of SP-211 were used. The specimens were previously tensile tested in an air environment at Pratt & Whitney Rocketdyne (PWR) in California. The J-2X engine was built by PWR under contract for NASA. The tensile specimens were conditioned at both 70°F and 750°F before they were pulled to failure. These tensile specimens included: (a) controls (as machined and thermally conditioned/annealed); (b) as-machined plus multiple cycles of 750°F thermal shock; and (c) thermal conditioning plus multiple cycles of 750°F thermal shock. Table 1 summarizes the tensile specimens tested at both 70°F and 750°F by PWR. A portion of the PWR samples in Table 1 were also tested at MSFC by the following techniques: (a) dynamic mechanical analysis (DMA), (b) porosity for larger material pores, (c) thermogravimetric analysis (TGA), (d) infrared spectroscopy (IR) and (e) differential scanning calorimetry (DSC).

EXPERIMENTAL METHODS

Materials Used and Sample Preparation

Each tensile specimen received from PWR was broken in the gage region after testing. The longest and widest rectangular strip was machined that included part of the gage region and one entire end tab. This rectangular sample was used for DMA testing in the three-point bending mode. Each rectangular sample was machined with a bench top low speed circular saw without the use of a coolant (so the sample was not contaminated).

Except for the rectangular sample tested as a function of temperature by DMA, the remainder of the tensile specimen was cut into 25-30 rectangular-to-cubic pieces with the low speed circular saw. It

was thought initially that these small pieces could be used for porosity testing. However, it was found that quality porosity testing was not possible without sufficient sample surface area. Sufficient surface area was obtained only by grounding the remaining Vespel SP-211 sample into a powder.

Figure 1 shows the types of sample preparation used with Vespel SP-211. On the left is a broken tensile specimen with two rectangular samples machined down the middle. For each specimen, the longer of the two rectangular samples was used for DMA testing. The middle of the photo shows the remainder of the tensile specimen machined into 25-30 small pieces of roughly equal size. These small pieces were later ground into a powder (right in photo) for porosity testing.

Grinding of each Vespel sample was performed with the SPEX 6700 Freezer/Mill. The grinding mechanism is a magnetic coil assembly suspended in a liquid nitrogen bath. Each sample was placed in a hard plastic grinding vial that has stainless steel caps on both ends. The vial is a cylindrical tube (0.875 in. diameter) with an effective length of 3 in. to contain the sample. A stainless steel rod impactor was placed in the vial with the sample. The impactor is a cylindrical rod 2.25 in. long and 0.375 in. diameter. The closed vial containing sample and impactor was inserted in the coil assembly. Liquid nitrogen was poured into the bath and 4-5 minutes were allowed for the cold vapor to subside. Each sample was then ground for 4 to 4.5 minutes at the maximum setting for impact frequency. In between grinding of samples, the vial interior and end caps were cleaned with isopropyl alcohol and dried with a clean tissue. Portions of each powdered sample were used for testing by porosity, TGA, IR spectroscopy and DSC.

Instruments Used

Dynamic Mechanical Analyzer (DMA)

The TA Instruments 2980 DMA was used for testing rectangular Vespel SP-211 samples with the three-point bend clamp. For three-point bending, the sample is not clamped at either end, and force is applied only on the middle of the sample at the location of the DMA drive shaft. Air was used as the sample atmosphere in the furnace, so the drive shaft was allowed to float on air bearings at a pressure of ~65 psi. The effective sample length was fixed at 20 mm by the clamp. An amplitude (displacement) of 30 μm and a frequency of 1 Hz were used to test each sample. Since three-point bend is a tensioning clamp, an initial static force of 0.1 N was programmed for each sample. Even though a low initial force was used, the loading force on the sample immediately increased at the start of each experiment and decreased with increasing temperature (the same trend as with storage modulus). The sample thermocouple was placed so it was only a few millimeters away from each sample edge. Each sample was programmed for 10 heat-cool cycles between 20 and 400°C (752°F) by the following experiment (~34 hours total):

1. Equilibrate and hold at 20°C for 5 min.
2. Ramp 4°C/min. to 400°C (752°F).
3. Isothermal at 400°C for 10 min.
4. Ramp 4°C/min. to 20°C.
5. Isothermal at 20°C for 5 min.
6. Repeat steps 1 to 5 for 9 more times.

Sample cooling during each DMA test was supplied with the TA Instruments Gas Cooling Accessory (GCA) that contained liquid nitrogen and provided cold gas to the DMA.

Surface Area and Porosity Testing

Surface area (small pores) and porosity (larger pores) were determined for samples of Vespel SP-211 (from PWR tensile specimens) that were ground into a powder with a freezer/mill. Determination

of surface area and porosity are based on physical adsorption of nitrogen gas molecules as a monolayer onto the material sample. This testing was performed with the Micromeritics TriStar™ 3000 Surface Area and Porosity System. This system allows the analysis of three material samples sequentially with a three-port sample manifold. Powdered SP-211 samples ranging from 0.50 to 1.45 g were degassed in a two-step process at 75°C (180 min.) and 130°C (1000 min.). The saturation pressure (P_o) of the nitrogen gas was determined in a separate tube. For each sample, the port was opened and nitrogen was allowed to adsorb onto the sample. The sample valve was then closed and the adsorption proceeded to equilibrium. Several measurements (8-9) of relative gas pressure (P/P_o) were made for each sample.

The BET equation models the measured number of moles (n) of nitrogen gas adsorbed onto 1 g of material adsorbent [2]. This equation assumes the adsorbed gas monolayer is in equilibrium with the vapor. If $1 / n [(P_o/P) – 1]$ is plotted vs. P/P_o, the slope and intercept allow calculation of the number of moles of gas adsorbed as a monolayer on 1 g of adsorbent (n_m).

Differential Scanning Calorimetry (DSC)

Portions of the powdered samples were also used for differential scanning calorimetry with a TA Instruments 2920 DSC. The DSC was used in the modulated mode, utilizing operating software to superimpose a sinusoidal heating rate over a slow underlying linear heating rate. The modulation allows more accurate determination of molecular transitions such as the heat of fusion (melting) of the PTFE Teflon component in Vespel SP-211 for estimating percent crystallinity. Each sample was heated from 25 to 400°C at an underlying heating rate of 0.9°C/min. with a modulation of ± 0.1°C every 40 sec. Each sample (8.8-9.1 mg) was mechanically crimped in a standard aluminum DSC pan and heated in an atmosphere of flowing argon gas.

Thermogravimetric Analyzer (TGA)

Portions of the powdered samples were also used for thermogravimetric analysis with a Thermo Scientific Thermogravimetric Analyzer (TGA). Each TGA sample was about 6 to 10 mg, and was heated in a flowing air combustion environment from 25 to 800°C at a heating rate of 10°C/min. Six Vespel SP-211 samples (including an as-machined control tensile tested at 70°F) were tested in duplicate by TGA. The decomposition onset temperature (of the polymer) was determined for each sample.

Infrared (IR) Spectroscopy

Infrared (IR) analysis was performed with a Nicolet/Nexus 670 Fourier Transform-Infrared (FT-IR) spectrometer. The IR analysis was performed at room temperature on portions of the same six powdered Vespel SP-211 samples that were tested by TGA. The IR analysis parameters were:

- single-bounce attenuated total reflectance accessory purged with nitrogen gas
- 64 scans per spectrum with a resolution of 4 cm^{-1}

A plot of infrared absorbance vs. wavenumber (cm^{-1}) was obtained for each sample.

RESULTS AND DISCUSSION

DMA Data

Figure 2 is a plot of storage modulus and temperature vs. time showing 10 heat-cool cycles for a Vespel SP-211 sample. Figure 3 is a plot of storage modulus and tan delta vs. temperature for the first heating scan of a Vespel sample. The peak maximum of tan delta (damping, energy loss) at 121°C likely indicates the alpha glass transition temperature for PTFE Teflon. The tan delta peak at 316°C likely indicates the onset of melting of PTFE [3].

Changes in Storage Modulus at 400°C vs. # of Heating Scans

Figure 4 is a plot of storage modulus at 400°C vs. heating scan # for Vespel SP-211 samples of as machined controls (ARC-4, -7) and thermally conditioned controls (CC-1, -3) that were tensile tested at 70°F and 750°F. 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. 4.

Figure 5 is a plot of percent change in storage modulus at 23°C and 400°C vs. heating scan # for as-machined control samples: ARC-4 (tensile tested at 70°F) and ARC-7 (tensile tested at 750°F). The percent change in modulus during ten DMA heating scans is based on the first heating scan. The increase in modulus for heating scan #'s 2-10 was greatest for the as-machined control sample tensile tested at 750°F.

For DMA heating scan #'s 2-10 for each Vespel sample, an increase in storage modulus ≥20% was determined to be undesirable. Considering that Vespel has some characteristics of a thermoset material, significant increases in modulus would lead to higher cross-link density and perhaps increased brittleness. A plot such as that shown in Fig. 5 was used as a basis for compiling DMA data in Table 2 for Vespel samples tested. Table 2 shows the DMA heating scan # (over a range of 2-10) at which the increase in storage modulus E' was >20% at 400°C. As-machined controls showed an increase in E' >20% at heating scans 3 and 6 for tensile testing at 750 and 70°F, respectively. As-machined material given multiple cycles of thermal shock showed the same increase in E' at heating scans 8 and 9 (for 5 and 2 thermal shocks tensile tested at 750°F, respectively). Thermally conditioned material tensile tested at 70°F showed the same increase in E' at heating scan 10—for a control as well as for 5 thermal shock cycles. The data in Table 2 perhaps indicates that thermal conditioning/annealing of the Vespel part before use would give it better thermal stability during repeated heat cycling up to 750°F.

Changes in Storage Modulus at 400°C for 10 min. vs. # of Heating Scans

While the effect of multiple DMA heating scans on storage modulus E' at 400°C was a concern, the effect on E' at 400°C for a 10-minute isothermal hold was also a concern. Figure 6 is a plot of storage modulus vs. time (10 min.) for sample ARC-4 (as-machined control tensile tested at 70°F). The modulus is shown for heating scan #'s 1, 2, 4, 6, 8 and 10. Most of the modulus increase during the 10-min. hold at 400°C occurred during heating scan #1 (max. 5.8% increase in E'). For subsequent heating scans, the increase in E' was no more than 1.4%. Figure 7 is a plot of percent change in storage modulus for 400°C/10 min. vs. DMA heating scan # (1-10). This plot is for control samples that were as machined and thermally conditioned, and were tensile tested at both 70 and 750°F. The as-machined control tensile tested at 750°F (ARC-7) had a maximum increase in E' of 6.6%, which was the most of any SP-211 sample held at 400°C for 10 min. The thermally conditioned control tensile tested at 750°F (CC-3) showed little to no change in E' for DMA heating scans 2-10. This indicates that thermal conditioning/annealing combined with some elevated temperature exposure at 750°F may provide even more thermal stability for the Vespel SP-211 material.

Relationship of Storage Modulus to Porosity of SP-211 Material

As described previously, porosity was determined for several powdered Vespel SP-211 samples with a surface area and porosity instrument. Figure 8 shows a plot of DMA storage modulus E' (1st heating scan only) vs. porosity for intermediate size material pores. Storage modulus was determined for each intact, machined rectangular sample in a category of thermal conditioning prior to tensile testing. A portion of sample remaining from the same category was ground into a powder with a freezer/mill for porosity testing. In Fig. 8, the smallest average pore diameters were for thermally conditioned control samples (CC-1, CC-3). The largest average pore diameters were for as-machined control samples (ARC-5, ARC-8). For the entire range of average pore diameters measured, samples

with multiple cycles of thermal shock (AR5X-7, AR10X-8 and C5X-4) were in about the middle of this range with average pore diameters of 314-321.5 Å. This middle range of pore diameters also corresponded to the highest values of storage modulus (~231.3k, 251.6k and 247.3k psi). Figure 8 indicates that as-machined controls of SP-211 were more vulnerable to higher porosity, while thermally conditioned controls yielded lower porosity (an advantage of annealing).

SUMMARY AND CONCLUSIONS

For specimens of Vespel SP-211 tensile tested following various levels of thermal conditioning at Pratt & Whitney Rocketdyne (PWR) in California, a portion of these broken tensile specimens were tested by a variety of techniques at NASA/Marshall Space Flight Center (MSFC) in Alabama. These various techniques—of which dynamic mechanical analysis (DMA) was prominent—were used to help prove the worthiness of SP-211 material for use on the Oxidizer Turbine Bypass Valve (OTBV) of the J-2X upper stage engine. The J-2X engine will be used on NASA's next heavy-lift vehicle for launching astronauts into deep space. The Vespel polyimide material would be exposed to multiple temperature cycles up to 750°F (399°C) in the OTBV during engine operation.

Rectangular DMA samples machined from broken PWR tensile specimens were given 10 controlled heat-cool cycles from 20 to 400°C. At the end of each heating scan for each sample, temperature was held at 400° for 10 min. before controlled cooling. An increase in DMA storage modulus E' >20% at 400°C was considered undesirable during heating scans 2-10 for each sample. A significant increase in modulus would lead to an increase in cross-link density and possible brittleness for a thermoset-like material such as SP-211. Vespel SP-211 material that was thermally conditioned/annealed did not have E' >20% until DMA heating scan #10, indicating that such thermal treatment gives the material more thermal stability and protection against significant modulus increases.

For exposure of each DMA sample to 400°C for a 10-min. hold, the greatest increase in storage modulus was 6.6% for all samples tested. The data for the isothermal hold at 400°C also indicated that thermal conditioning/annealing of SP-211 combined with some exposure to 750°F may provide even more thermal stability and protection against a significant modulus increase.

ACKNOWLEDGMENTS

The author would like to acknowledge several individuals who supplied material samples or performed testing on Vespel SP-211 for this effort. Raul Perez at Pratt & Whitney Rocketdyne (PWR) supplied broken tensile specimens. Some of these specimens were machined into rectangular DMA samples at NASA/MSFC, and others were ground into a powder at MSFC for DSC, porosity, TGA and IR testing/analysis. Diep Trinh (Nonmetallic Materials and Manufacturing Division) performed porosity and surface area testing on powdered Vespel samples at MSFC. Richard Boothe (Materials Test Branch) performed TGA testing and IR spectroscopy on powdered Vespel samples at MSFC.

REFERENCES

1. "Properties of DuPont VESPEL® Parts," DuPont Engineering Polymers, August 1993.
2. Brantley S. L., Mellott, N. P., Amer. Mineralogist, 2000, 85, 1767-1783.
3. Brandrup, J., Immergut, E. H., editors, Polymer Handbook, 3rd ed., New York: Wiley & Sons, 1989, Section V, pp. 39, 41.

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

NOTES:

- One thermal conditioning cycle: Heat (anneal) material at 1.5°C/min. to 399°C (750°F), and hold at 750°F for 1 hour. 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.

Table 2. Effect of prior tensile testing history on stability of DMA storage modulus at 400°C for 2 to 10 heating scans.

Prior tensile testing history of sample used in DMA	# of DMA heating scan (out of 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

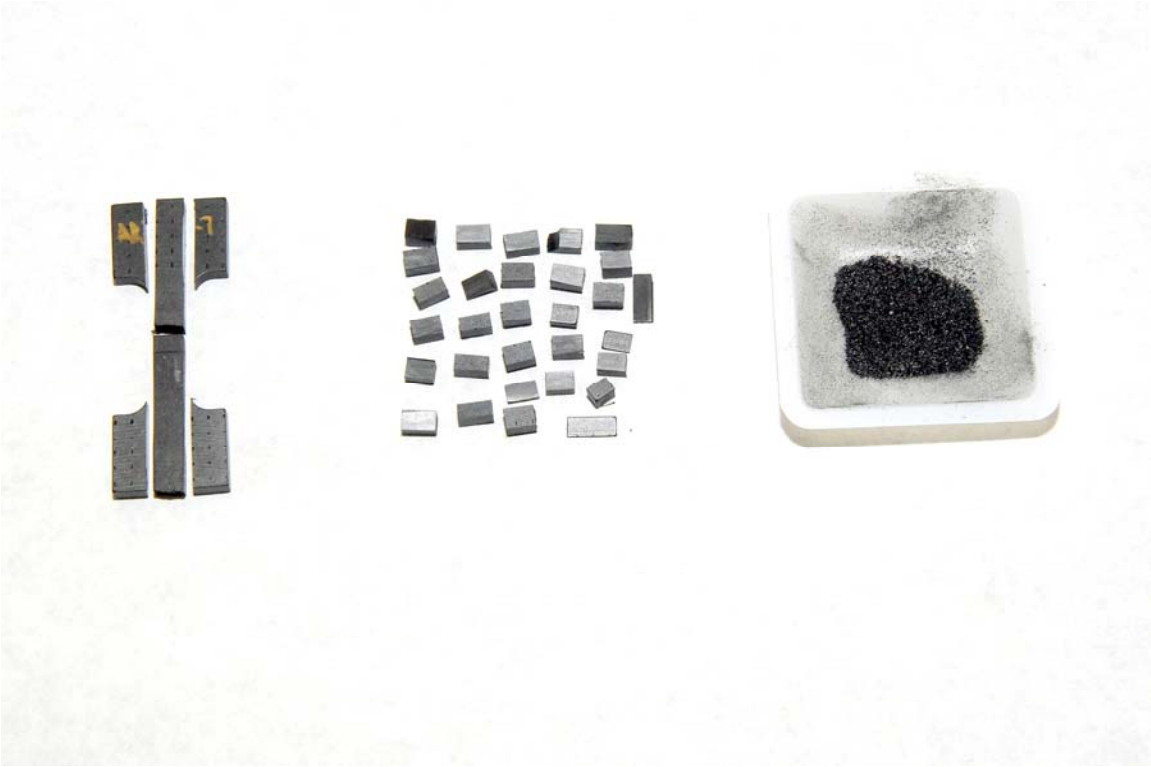

Fig. 1. Steps in sample preparation for various tests on Vespel SP-211:

Left—Broken tensile specimen from 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 saw.

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

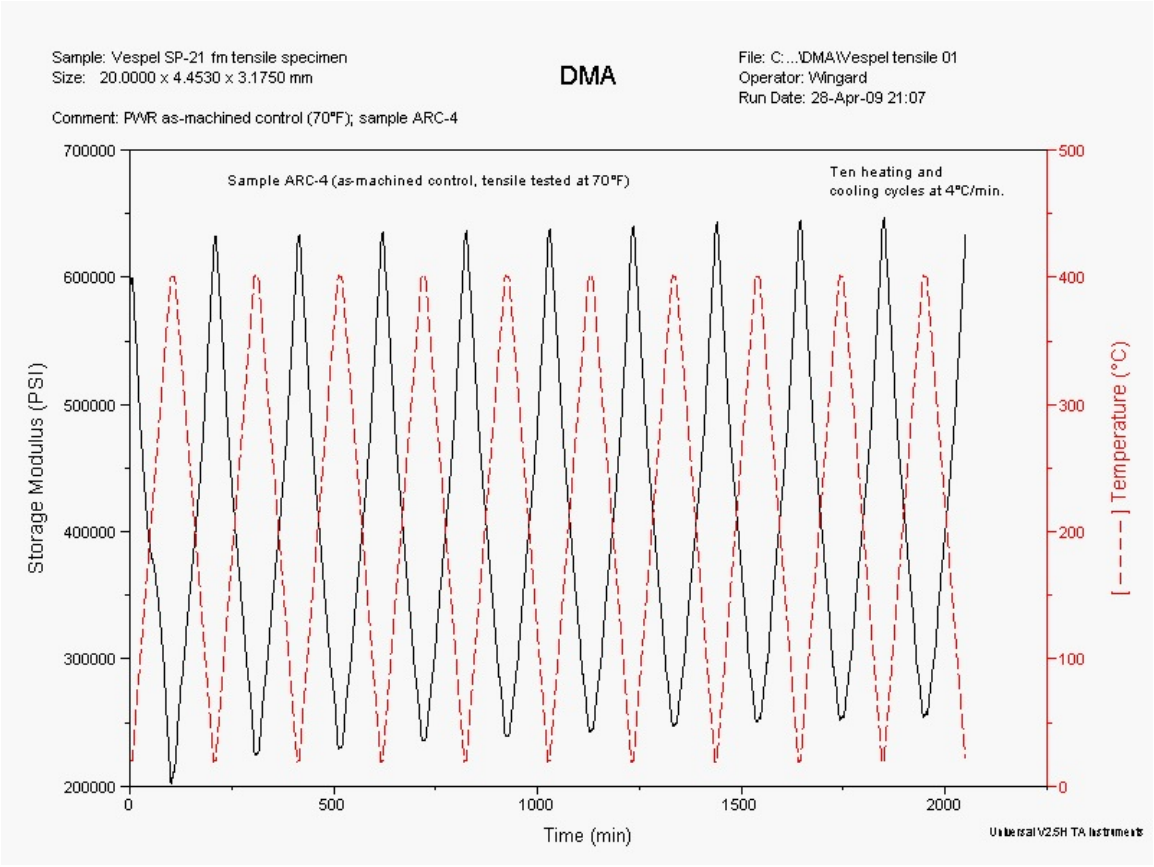

Fig. 2. DMA plot of storage modulus and temperature vs. time for 10 heating and cooling scans on a sample of Vespel SP-211 (ARC-4, as-machined control tensile tested at 70°F). Each scan covered 20-400°C at 4°C/min., with a 10-min. hold at 400°C at the end of each heating scan. The sample was tested with the DMA three-point bend clamp.

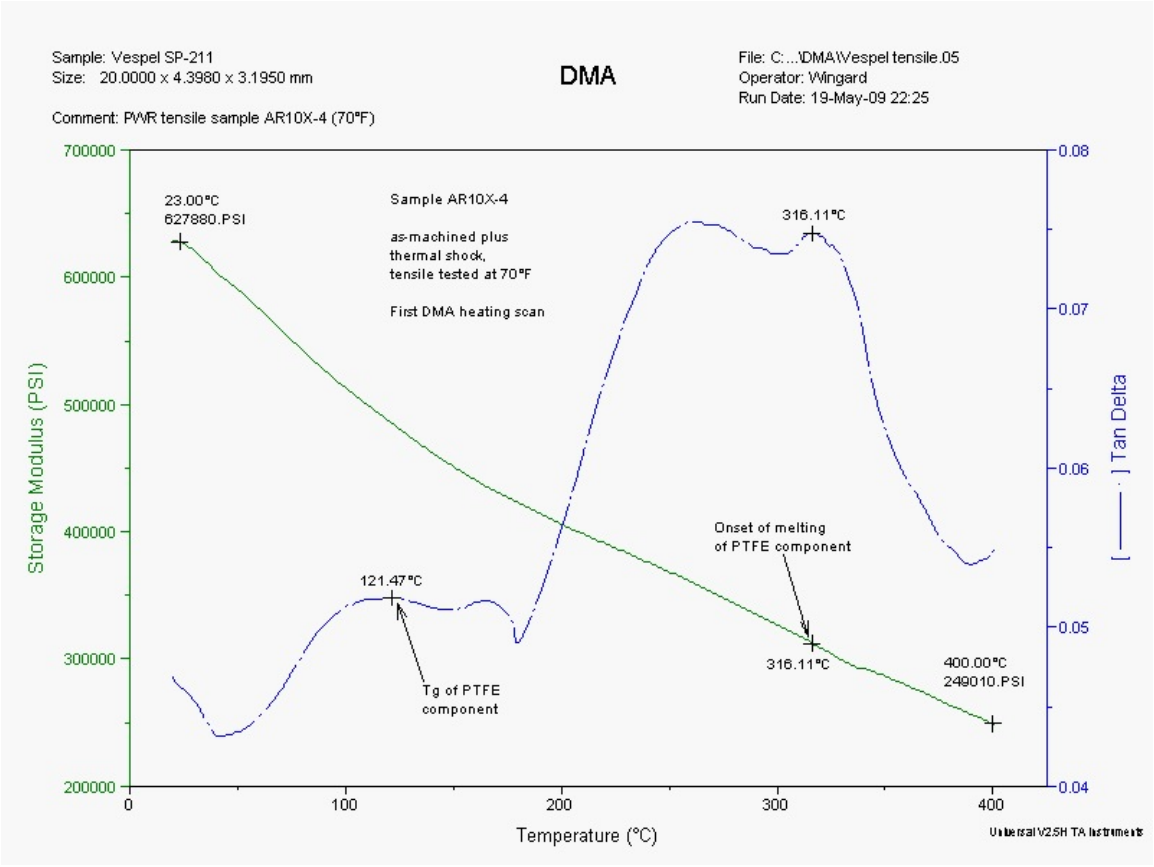

Fig. 3. DMA plot of storage modulus and tangent delta (energy loss damping peak) vs. temperature for a Vespel SP-211 sample (AR10X-4, as-machined + 10 cycles of 750°F thermal shock). This is a plot for the first heating scan only. Tan delta peaks at 121°C and 316°C are for molecular transitions of the PTFE Teflon component in SP-211: alpha glass transition temperature (Tg) and onset of melting temperature (Tm), respectively.

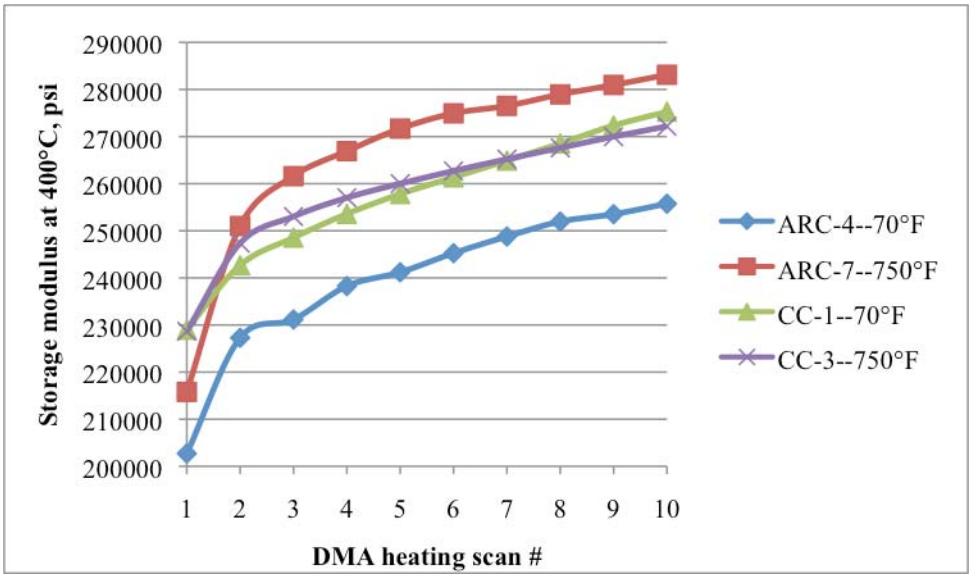

Fig. 4. DMA plot of storage modulus at 400°C vs. heating scan # for as-machined controls (ARC-4, -7) and thermally conditioned controls (CC-1, -3) that were tensile tested at 70°F and 750°F.

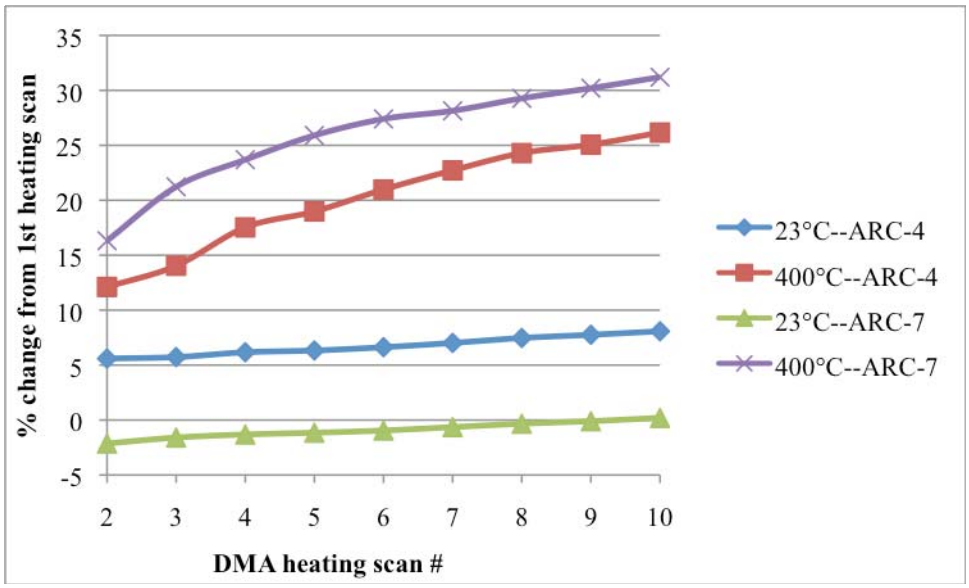

Fig. 5. Percent change in DMA storage modulus (based on 1st heating scan) vs. heating scan # at 23°C and 400°C for as-machined control samples: ARC-4 (tensile tested at 70°F) and ARC-7 (tensile tested at 750°F).

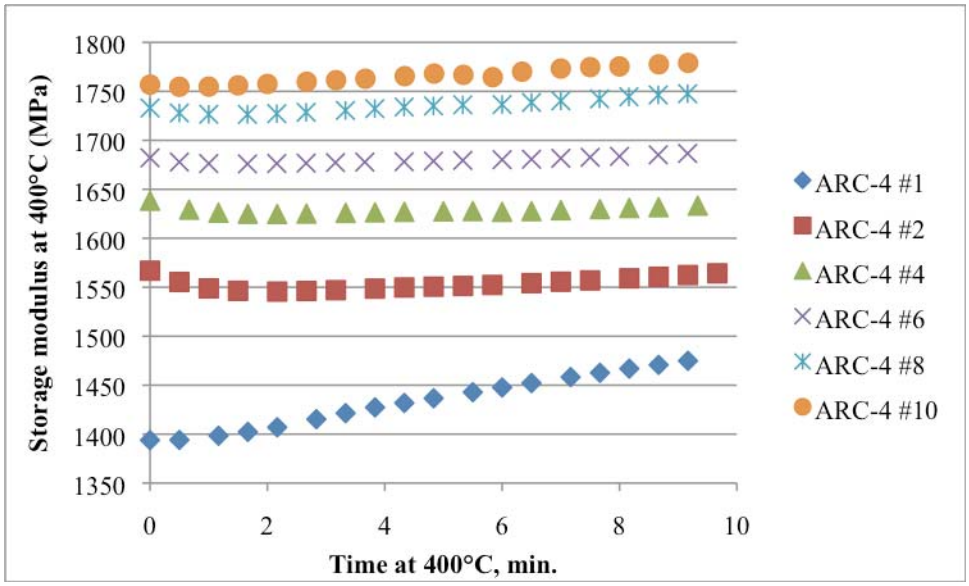

Fig. 6. DMA storage modulus at 400°C vs. time at 400°C (0-10 min.) for sample ARC-4 (as-machined control tensile tested at 70°F). Modulus vs. time curves are shown for DMA heating scan #'s 1, 2, 4, 6, 8 and 10.

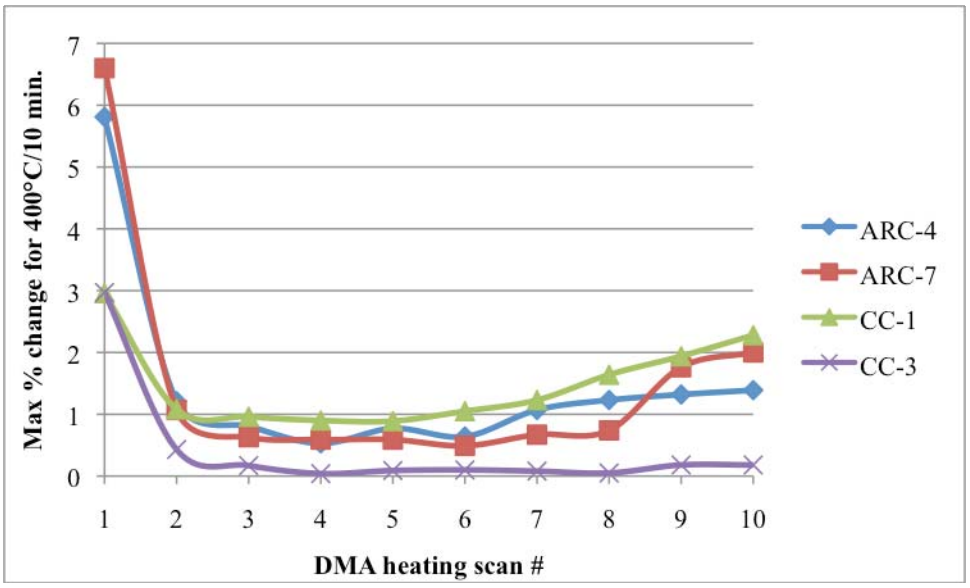

Fig. 7. Percent change in DMA storage modulus (400°C/10 min.) vs. heating scan # for Vespel SP-211 control samples: as machined (ARC-4, -7 tensile tested at 70 and 750°F) and thermally conditioned (CC-1, -3 tensile tested at 70 and 750°F).

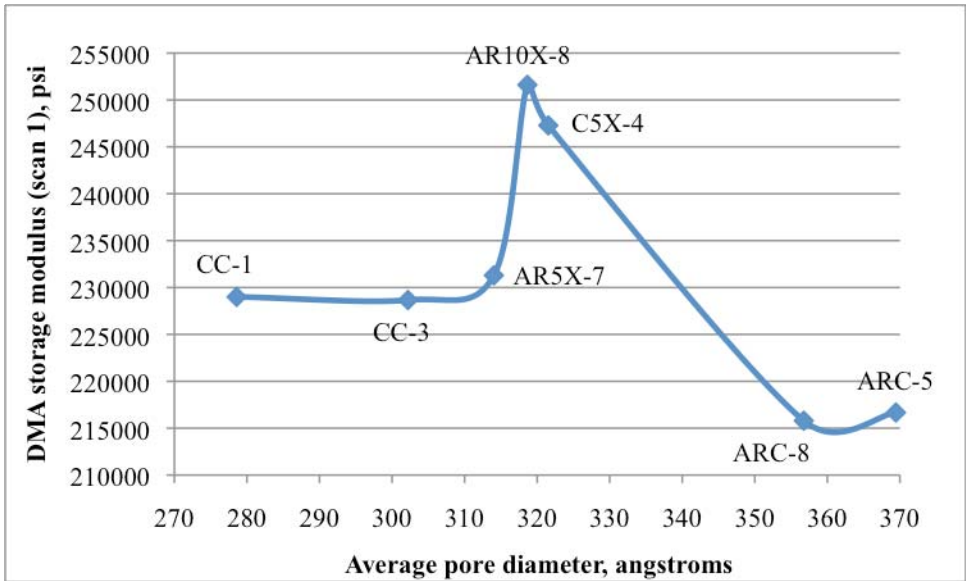

Fig. 8. DMA storage modulus (from 1st heating scan) vs. porosity (avg. pore diameter of intermediate-to-larger pores) for several powdered samples of Vespel SP-211.

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)