

# **DMA Modulus as a Screening Parameter for Compatibility of Polymeric Containment Materials with Various Solutions for Use in Space Shuttle Microgravity Protein Crystal Growth (PCG) Experiments**

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## **ABSTRACT**

Protein crystals are grown in microgravity experiments inside the Space Shuttle during orbit. Such crystals are basically grown in a five-component system containing a salt, buffer, polymer, organic and water. During these experiments, a number of different polymeric containment materials must be compatible with up to hundreds of different PCG solutions in various concentrations for durations up to 180 days. When such compatibility experiments are performed at NASA/MSFC simultaneously on containment material samples immersed in various solutions in vials, the samples are rather small out of necessity. DMA modulus was often used as the primary screening parameter for such small samples as a pass/fail criterion for incompatibility issues. In particular, the TA Instruments DMA 2980 film tension clamp was used to test rubber o-rings as small in I.D. as 0.091 in. by cutting through the cross-section at one place, then clamping the stretched linear cord stock at each end. The film tension clamp was also used to successfully test short length samples of medical/surgical grade tubing with an O.D. of 0.125 in.

## **INTRODUCTION**

Space Shuttle experiments in orbit have yielded evidence that the low-gravity (microgravity) environment of space can produce crystals of larger size, better shape and higher quality than those obtained on Earth. Such experiments also show that benefits from microgravity crystal growth can be crucial to success in protein structure determination. One of the primary research efforts to use microgravity to grow protein crystals for commercial products is in drug design. One product that is working toward market readiness is a treatment for influenza. Ongoing research shows that protein crystals grown in space also have commercial potential in the treatment of heart disease, diabetes, cancer, HIV and emphysema (1).

Many different solutions can be used to produce protein crystals in space, and these solutions must be compatible with their containment materials for durations up to 180 days. This paper focuses on the use of thermal analysis techniques, particularly DMA, as a screening parameter in compatibility studies at NASA/MSFC.

## **EXPERIMENTAL**

### Containment Materials for PCG Solutions

The Nonmetallic Materials & Processes Group/ED34 at NASA/MSFC has tested a number of different polymeric containment materials after removal from the various PCG solutions, and the materials are summarized in Table 1 along with the type of testing used. In all testing, conditioned material samples were compared with control (virgin) samples.

### Compatibility Experiments of Containment Materials in PCG Solutions

Samples of containment materials were immersed in the various PCG solutions in glass vials, and conditioned by accelerated exposure at 42°C. This work was performed by the Chemistry Group/ED36 at NASA/MSFC. The accelerated exposure was necessary for meeting Shuttle flight schedules, and was determined to be the equivalent of minimum and maximum test durations of 120 days (A-test) and 180 days (B-test) at 22°C. So far, each of the containment materials has been conditioned in almost 200 PCG solutions covering three phases of work. After removal of each material sample from the solution, it is allowed to dry and is measured for weight changes or volume swell. Each sample is then photographed by ED36 with a digital camera attached to a microscope, to observe for possible surface pitting or crazing/cracking. The samples are then delivered to ED34 for further testing. For irregularly-shaped samples cut from actual PCG housing, only hardness testing was possible followed by some DSC thermal analysis testing. Flat sheet material was preferred for ease of testing, and was normally machined into samples 2 in. x 0.5 in. x 0.125 in. These rectangular samples were tested for modulus (stiffness) changes by DMA.

### Thermal Analysis Testing by DMA and DSC

For the containment material samples removed from the PCG solutions, the primary testing was performed with the TA Instruments 2980 DMA by heating samples from 20 to 45°C at 3°C/min. Small rubber o-rings (Table 1) were tested in the DMA film tension mode by cutting through the o-ring cross-section at one place, then clamping the stretched linear cord stock at each end. Short lengths (0.75-1.0 in.) of Tygon® tubing (Table 1) were also tested by DMA film tension. For the o-ring and tubing samples, the following parameters were used for film tension: frequency = 1 Hz; static force = 0.1 N; amplitude = 30-40 µm; auto-strain = 120%; and sample torque ≈ 1-2 in.-lbs. Some of the tubing samples were made unusually stiff by the PCG solutions, and for these the amplitude was reduced to 5 µm. Rectangular samples cut from flat sheet rigid plastic material were tested with the DMA 20 mm double cantilever clamp. In this mode, the following parameters were used: frequency = 1 Hz; amplitude = 15 µm; and sample torque ≈ 8 in.-lbs. It was necessary that some of the Lexan® 9600 samples be tested in the single cantilever mode, and this required an amplitude = 40 µm. The PIG® Mat polypropylene absorbent mat material (Table 1) is unique in that it has eight layers held together by plastic fasteners. It was found that the only quality test data on these mat samples could be obtained with DMA film

tension. The outermost layer ( $\approx 0.18$  mm thick) was peeled from the mat sample and was tested with the same DMA parameters as for the o-rings.

For irregularly-shaped samples cut from actual PCG housing, DMA modulus testing was not possible. Some of these samples were tested with the TA Instruments 2920 DSC in the modulated mode. Each DSC sample was cut as a thin surface slice with a low-speed circular diamond edge saw, and was crimped in a non-hermetic aluminum DSC pan. Each sample was heated from 22 up to 300°C at an underlying linear heating rate of 5°C/min., with an argon gas purge. A modulation of  $\pm 0.636^\circ\text{C}$  every 60 sec was used.

## RESULTS AND DISCUSSION

### O-Ring and Tubing Sample Data

The primary screening parameter for the 2-020 size o-rings was tensile testing on an Instron machine at 70°F. Each o-ring cut through the cross-section at one place was clamped at each end with 30-40 psi pressure grips, and pulled to tensile failure at a crosshead speed of 20 in./min. O-rings considerably smaller than the 2-020 size (Table 1) could not be tested on the Instron, and were tested only in the DMA film tension mode. Some of the 2-020 size o-rings that were tensile tested were also tested for DMA film tension modulus. Fig. 1 shows the correlation between maximum tensile stress and DMA modulus for Viton V747-75 and Nitrile (Buna N) o-ring materials. Compared to the Viton material, the Nitrile material is shown to be more susceptible to greater increases in modulus. Fig. 1 does not match the same set of PCG solutions for both o-ring materials. However, DMA film tension testing on smaller Nitrile o-rings from Phase I solutions showed that modulus values would predict a curve of the same shape as in Fig. 1. Most of the o-rings were tested for compatibility with the PCG solutions as both lubricated (with an appropriate grease) and dry. The test data shown in Fig. 1 is for dry o-rings. It was found that lubrication of the o-rings did not have much effect on the tensile or modulus data.

For Tygon tubing samples in Phase I-III solutions for A-test and B-test durations, 12 of these were found to be extraordinarily stiff. The average DMA modulus at 22°C for the virgin tubing material was 1,754 psi. However, these very stiff samples had moduli ranging from about 14,000 to 170,000 psi at 22°C for the B-test duration. This modulus increase was accompanied by shrinkage in the tubing O.D. of up to 12% for the B-test duration. The concentrations of these solutions were later reduced considerably to lower the modulus values to a more acceptable range. Fig. 2 shows that for a modulus range of about 10,000 to 200,000 psi, there was a good linear fit of the tubing data as a semi-log plot of DMA modulus vs. tubing O.D., for both the A-test and B-test durations.

### Rectangular Plastic Sample Data

From Table 1, two amorphous thermoplastics were tested extensively in the DMA double cantilever mode for both A-test and B-test durations: two grades of Lexan® polycarbonate (940A, 9600) and Udel® polysulfone P-1700. There was a slight reduction in the storage modulus at 22°C of these

thermoplastics after the B-test duration. With only a few exceptions, these thermoplastics were largely unaffected by the PCG solutions, with most of the samples having about 85 to 109% of the modulus of the virgin material after the B-test. What is not reflected in this modulus data is that the polysulfone samples from two of the solutions (acetonitrile, 40% v/v; and hydroxycoumarin, 43.8 mM) had severe cracking/crazing after the B-test, which is unacceptable for PCG use.

Fig. 3 shows that modulus data was also obtained in the DMA double cantilever mode for a semi-crystalline thermoplastic, Nylon 66 (MS 18212-25). The results for Nylon 66 were much more negative, as most of the samples tested with 41 PCG solutions had only about 35 to 55% of the modulus of the virgin material after the B-test. Reduction to less than 40% of the virgin material modulus after the B-test was considered unacceptable, and this was the case for Nylon 66 in 12 of the PCG solutions. Fig. 3 shows that HCl (1.0 M) solution severely attacked the Nylon 66 after the B-test, reducing the modulus by 95.5% and causing extensive cracking and crumbling.

## CONCLUSIONS

The compatibility of polymeric containment materials with various protein crystal growth (PCG) solutions was determined for use in Space Shuttle experiments up to a 180-day duration. DMA modulus was used as a primary screening parameter to determine if some material/solution combinations were unacceptable. For rubber o-rings of sufficient size, Instron tensile strength was the primary screening parameter for determining acceptable compatibility, along with significant o-ring volume swell and observed surface pitting. However, for Viton® o-ring material, only 5 of almost 200 PCG solutions were deemed unacceptable by such criteria. Further correlations were made between tensile strength and DMA modulus for Viton and Nitrile elastomers.

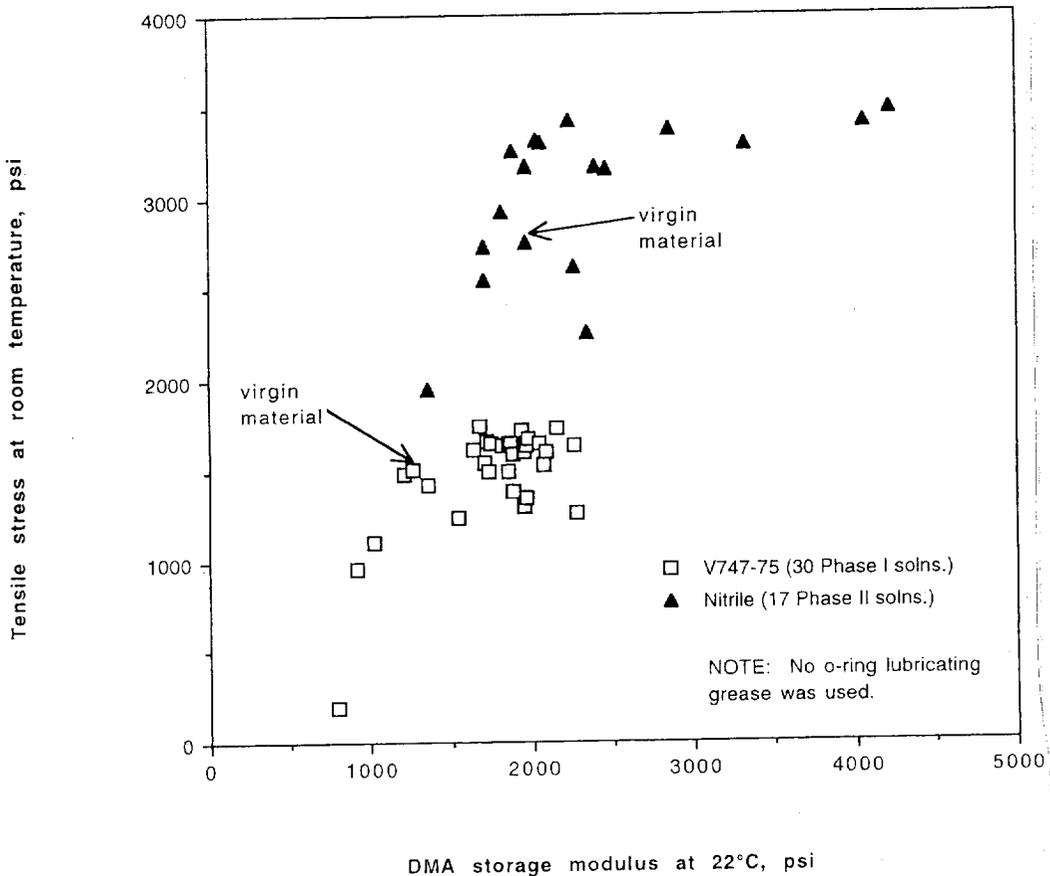
Rectangular samples machined from flat sheet of various thermoplastics were also tested for compatibility with PCG solutions by DMA modulus. Two amorphous thermoplastics—polycarbonate (two grades) and polysulfone—had mostly good compatibility with the PCG solutions, with only 6 solution/material combinations considered unacceptable. For Nylon 66, a semi-crystalline thermoplastic, the DMA modulus data was much more negative. Reduction to less than 40% of the virgin material modulus after the B-test was considered unacceptable, and this was the case for Nylon 66 in 12 of the PCG solutions

## REFERENCES

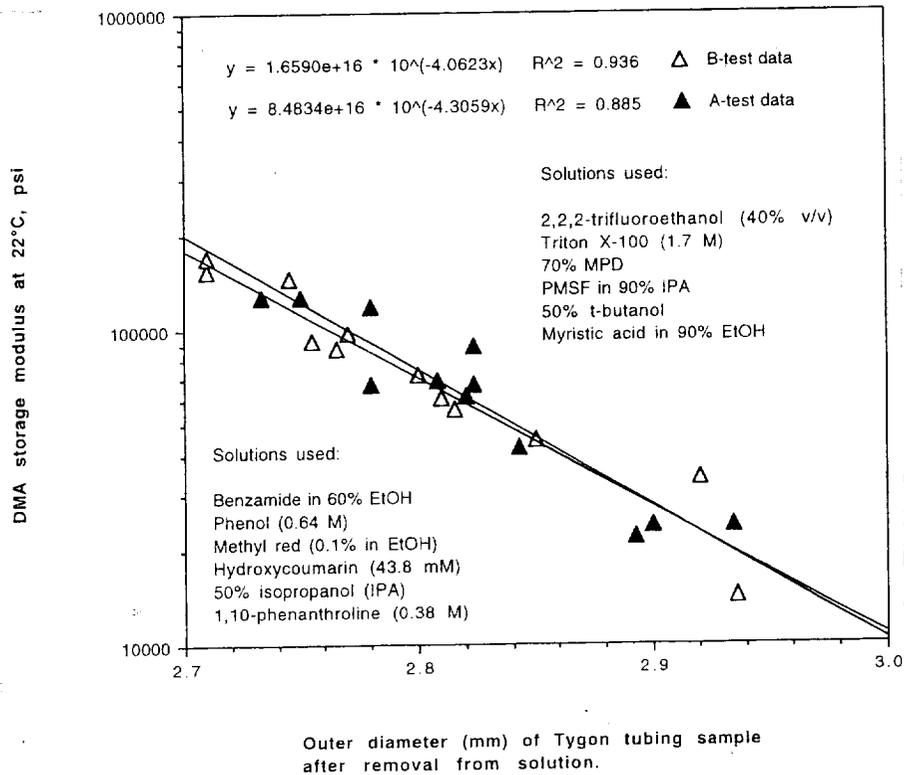
1. NASA/MSFC web site for Microgravity—Biotechnology/Protein Crystal Growth (<http://microgravity.msfc.nasa.gov/pcg.html>).

Polymeric Material	Sample Type and Size	Testing Technique Used
Viton® fluorocarbon elastomer (Parker V747-75, V680-70)	2-020 size o-rings (I.D. = 0.864 in., C/S = 0.070 in.)	Tensile (Instron) & DMA film tension
Nitrile (Buna N) elastomer (70 hardness)	O-rings: 2-020 size O-rings: I.D. x C/S (in.) = 0.264 x 0.032	Tensile, DMA film tension DMA film tension
Neoprene® (CR) elastomer (70 hardness)	O-rings: 2-020 size O-rings: I.D. x C/S (in.) = 0.091 x 0.059	Tensile DMA film tension
Tygon® S-50-HL medical/surgical elastomer	Tubing: O.D. = 1/8 in., I.D. = 1/16 in.	DMA film tension
PIG® Mat polypropylene absorbent mat (MAT 204)	Eight layers of material held together by fasteners.	DMA film tension
Nylon 66 (MS 18212-25, ASTM D4066)	Screws 1/8-in. thick sheet material	Hardness, MDSC® DMA double cantilever
Lexan® polycarbonate (940A and 9600)	Housing material (940A) 1/8-in. thick sheet material (940A, 9600)	Hardness, MDSC® DMA double cantilever
Udel® polysulfone (P-1700 and P-3703)	Syringe material (P-3703) 1/8-in. thick sheet material (P-1700)	Hardness, MDSC® DMA double cantilever
Black Delrin® 100 acetal	1/8-in. thick sheet material	DMA double cantilever
Zeonex® E48R cyclo-olefin polymer	Housing material	Hardness, MDSC®
Plexiglas® G acrylic	1/8-in. thick sheet material	DMA double cantilever

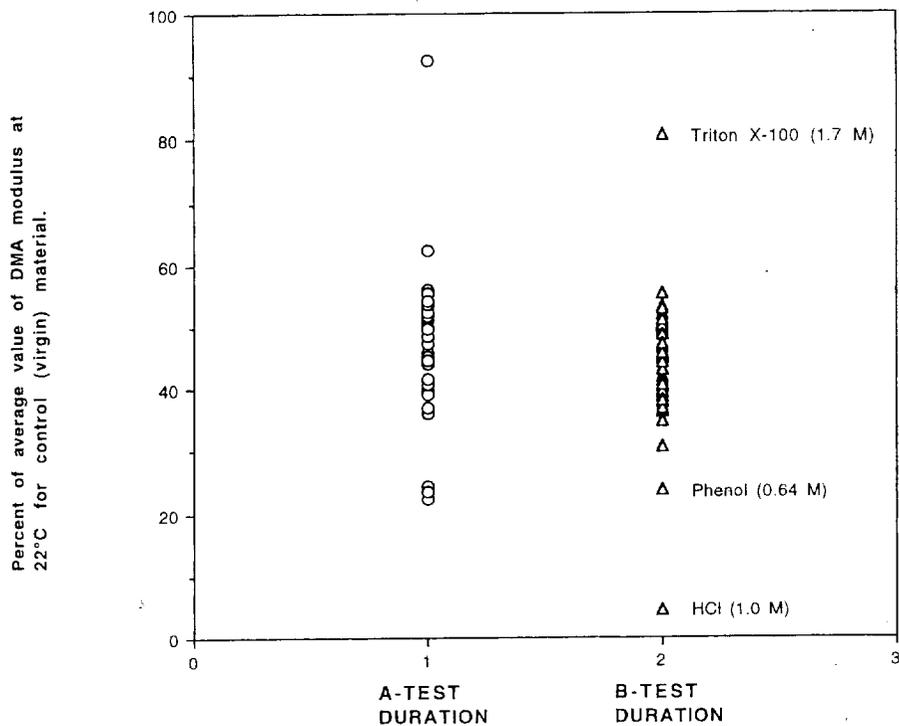
**Table 1.** Several polymeric containment materials tested for compatibility with PCG solutions by thermal analysis and other techniques.



**Fig. 1** Tensile stress vs. DMA modulus for size 2-020 o-rings of Viton V747-75 and Nitrile in Phase I & II solutions for A-test duration only.



**Fig. 2** DMA modulus vs. sample O.D. for Tygon® tubing (S-50-HL) in 12 Phase I-III solutions for A-test and B-test durations.



**Fig. 3** Changes in DMA storage modulus at 22°C for Nylon 66 sheet samples in 41 Phase II & III solutions for A-test and B-test durations.