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USE OF THE TMA FILM TENSION TECHNIQUE FOR DIFFERENTIATING POLYMERIC MATERIALS IN THE SPACE SHUTTLE PROGRAM

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Abstract

During the recent processing of a forward segment of the Reusable Solid Rocket Motor (RSRM) for the Space Shuttle, the topcoat white paint turned light brown after autoclave cure of the case insulation. Thermomechanical analysis (TMA) in the film tension mode produced modulus *vs.* temperature data that helped to explain why a certain insulation vacuum bagging material contributed to the brown paint color. TMA film tension data was also obtained on lab-created white and brown topcoat paint samples (with and without primer). The brown/white ratios of moduli were about 2/1 and 4/1 for topcoat/primer and topcoat only samples, respectively, from 25 to 55°C.

Keywords: accelerated aging, brown paint anomaly, RSRM segment, TMA film tension, vacuum bag material

Introduction

The exterior of the RSRM case segments are painted with a Rust-Oleum two-component, high gloss polyamide converted epoxy finish topcoat over a Rust-Oleum primer. All painted surfaces on the RSRM segments tend to slightly discolor during normal cure of case insulation. During the recent processing of a forward segment of the RSRM, however, the entire white topcoat turned light brown following insulation cure. Since this segment of the Space Shuttle Solid Rocket Booster (SRB) is forward of the Orbiter's crew compartment, there was some concern that the brown paint could produce potentially dangerous paint debris during flight. Surface analysis testing of the brown paint samples at Thiokol/Wasatch (TC/W) in Utah showed that they contained up to 2% sulfur (0.2% is normal). Sulfur is present in the rubber case insulation as part of the cure mechanism, and virtually all of the sulfur volatiles are removed by the vacuum system during normal autoclave cure. Vacuum pressure traces by TC/W from the autoclave cure showed that the vacuum level was no worse than about 3 in. Hg higher than normal level of historical vacuum data for autoclave cure of RSRM forward segments. For the brown paint anomaly, this was the first time use of a particular Nylon vacuum bagging material around the insulation during cure. Differential scanning calorimetry (DSC) temperature scans by TC/W on this bag material (and several previously used bag materials) showed that the new bag material had a melting point onset near that of the insulation cure temperature of 146°C. It was a lower melting point onset than was

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observed on the earlier bag materials (which could be related to types, sizes and arrangements of crystallites). We believe the brown paint color was attributed to sulfur from the insulation permeating through the new vacuum bag material during the autoclave cure, with the sulfur reacted with some binder(s) in the paint.

The Nonmetallic Materials Branch at the NASA/Marshall Space Flight Center (MSFC) supported the brown paint investigation by using a thermomechanical analyzer (TMA) in the film tension mode to test the following materials: (1) new and previously used RSRM vacuum bag materials; and (2) lab-created white and brown topcoat paint samples (with and without primer).

Experimental methods

Vacuum bag samples and paint samples were supplied to NASA/MSFC by TC/W. Several virgin vacuum bag material samples were supplied: (a) SL-800 (the new material that resulted in the brown paint); (b) HS-800; (c) HS-8171; and (d) DP-1000. Bagging materials (b), (c) and (d) have all been used in previous RSRM case insulation cures. A sample of SL-800 used in the autoclave cure that produced the brown paint was also supplied. Lab-created white and brown topcoat paint samples (with and without primer) were sprayed on 10.2×30.5 cm (4×12 in.) flat steel panels and cured. The brown color was recreated when the paint panels were cured in the presence of the rubber insulation. We were informed by TC/W that the lab-created light brown paint was slightly darker than that on the RSRM forward segment. The paint samples were sprayed over a Teflon tape base on the steel panels, to allow for easy specimen removal for the TMA tests.

The TA Instruments 2940 TMA was used in the film tension mode for determining the modulus (stiffness) of the vacuum bag and paint specimens as a function of temperature. The modulus for each specimen was calculated from the initial slope of stress/strain data (based on force/dimension change data from the TMA 2940). The TMA specimens were cut as rectangular strips about 4.8×19.1 mm (0.188×0.75 in.). Vacuum bag TMA specimens averaged about 0.06 mm thickness. Topcoat paint/primer TMA specimens averaged about 0.11 mm thickness; the topcoat paint only specimens about 0.05 mm thickness. The following TMA test method was used for testing the vacuum bag specimens, with an argon gas purge for each specimen:

1. Equilibrate at 25°C.
2. Force at 0.05 Newtons (N).
3. Ramp force 0.05 N min^{-1} to 1.0 N.
4. Increment 15°C.
5. Repeat segment 2 till 160°C.

The same TMA test method above was used for testing the paint specimens, except that step 3 was changed to:

3. Ramp force 0.05 N min^{-1} to 0.8 N.

Due to these lengthy TMA experiments (each test took about 2.5 h), no repeat TMA scans were performed per specimen for "conditioning" the specimen. The initial film tension tests performed on the paint specimens were for the paint sample panels exposed to ambient lab conditions. Later film tension tests were also performed on paint specimens exposed to an elevated temperature (41°C/105°F) and extremes in relative humidity (RH, 26% and 87%). Humidity "chambers" were created by placing white and brown topcoat/primer and topcoat only specimens on a platform inside a sealed empty glass desiccator, then placing the two chambers in different forced-air ovens for an eight-week exposure time. The low humidity chamber was created with a beaker of a saturated solution of hydrated potassium fluoride ($KF\cdot 2H_2O$) in distilled water. The high humidity chamber was created simply with a beaker of distilled water. Average %RH values over the eight-week period were obtained by periodically placing an RH indicator inside each desiccator for a 24-h period.

A TA Instruments 910 DSC was also used to analyze several vacuum bag and paint specimens, with a heating rate of 10°C min^{-1} and an argon gas sample purge. For each type of specimen, two layers of material were used for yielding a DSC specimen size of 4.5–4.8 mg.

Results and discussion

For the different vacuum bag materials tested by the TMA film tension technique, a plot of modulus *vs*. temperature is shown in Fig. 1. With increasing temperature, the virgin SL-800 vacuum bag material had the lowest modulus of the materials tested, especially approaching the temperature for autoclave cure of RSRM case insulation (146°C/295°F). This data helps to explain why the pliable SL-800 material was permeable to sulfur at the insulation cure temperature. The TMA

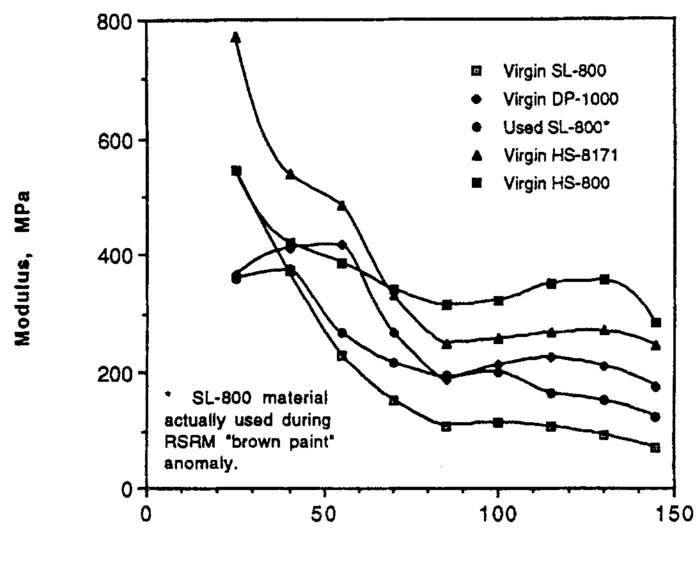

Fig. 1 TMA moduli *vs*. temperature for several RSRM vacuum bagging materials

specimen of SL-800 material taken from the insulation vacuum bag used in the brown paint anomaly showed a higher modulus with increasing temperature than the virgin material. Because of the ability of the various TMA vacuum bag specimens to stretch with increasing temperature, none of these specimens broke from 25 to 160°C.

For paint samples exposed to ambient laboratory conditions, the TMA topcoat/primer specimens were tested over a TMA force range of 0.05–0.8 N. This force range allowed the topcoat/primer and topcoat only specimens to not break until 160°C and 130°C, respectively. The maximum strain at break for the topcoat/primer and topcoat only specimens was about 0.05 and 0.35, respectively, regardless of sample color. At TMA "ambient conditions" (25°C), the maximum strain (not at break, but at 0.8 N) was greater for the white specimens by a factor of two over the brown specimens for both specimen types. Figure 2 shows a plot of stress *vs.* strain at 25°C for white and brown topcoat/primer specimens, and the yield point is clearly evident for the white specimen.

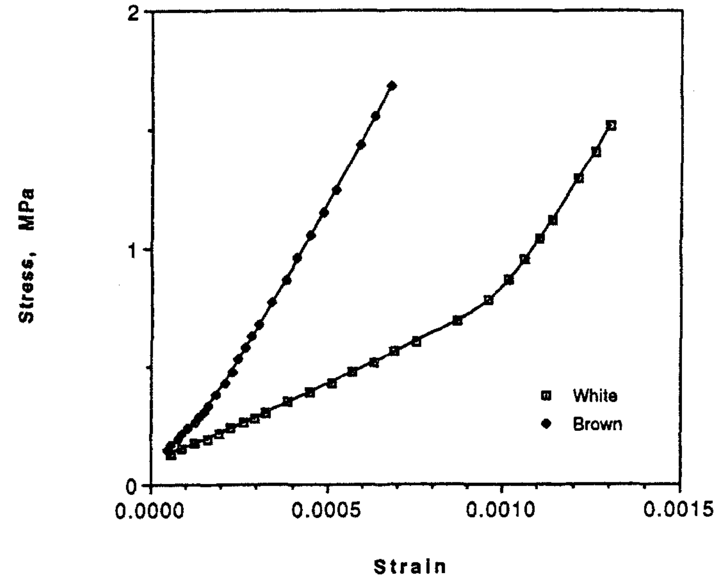

Fig. 2 TMA stress *vs.* strain at 25°C for brown and white samples of topcoat plus primer exposed to ambient laboratory conditions

For paint samples exposed to ambient lab conditions, Fig. 3 shows a plot of modulus *vs.* temperature for topcoat/primer and topcoat only TMA specimens for the two topcoat colors. The brown/white ratios of moduli were about 2/1 and 4/1 for topcoat/primer and topcoat only specimens, respectively, from 25 to 55°C. From 25 to 55°C, the moduli of the brown specimens were similar, with and without the primer. Over the same temperature range, however, the moduli of the white specimens were about two times higher for topcoat/primer than for topcoat only. This indicates that the primer is at least as stiff as the normal white topcoat paint,

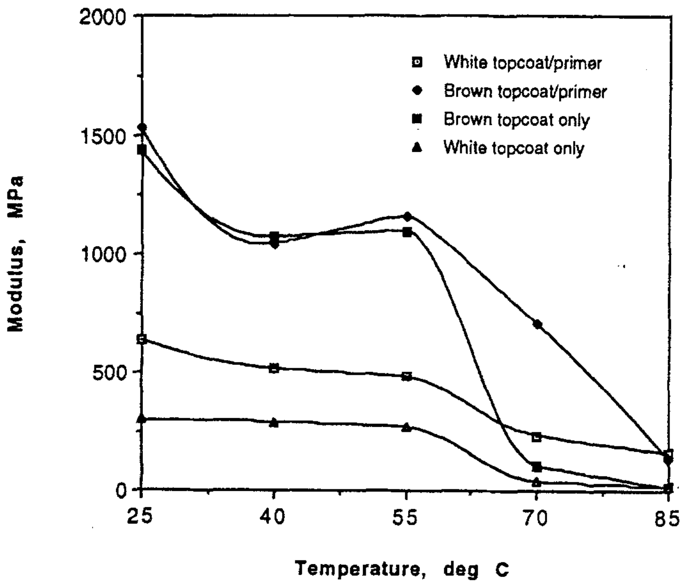

Fig. 3 TMA moduli *vs*. temperature of topcoat/primer and topcoat only samples (brown and white) exposed to ambient laboratory conditions

although no film tension data was obtained on the primer alone. Above 55°C, Fig. 3 shows that the modulus for each paint specimen decreased dramatically due to the glass transition temperature (T_g) of the paint. DSC data indicated the topcoat T_g more accurately as 61°C. At temperatures ≥85°C, the moduli of the brown and white specimens were about equal for each specimen type.

Significant testing on the brown paint anomaly was performed at TC/W in Utah. Microhardness data showed that the brown paint was 20–30% harder than the white paint, which complimented the modulus data from NASA/MSFC. Shore A hardness measurements on the case insulation in the RSRM forward segment indicated that the rubber cured properly, and thickness and X-ray measurements on the cured insulation showed no presence of unacceptable voids. Tensile adhesion data on brown and white topcoated panels after accelerated aging showed nominal values. For the RSRM forward segment, NASA/MSFC and TC/W agreed that for critical bonding surfaces, the brown topcoat would be removed/abraded with subsequent re-application of the normal white topcoat. For case acreage regions on the hardware, the brown paint would be encapsulated by a cosmetic white topcoat at final assembly.

Following the disposition of the flight hardware, additional film tension data was obtained at NASA/MSFC for topcoat/primer and topcoat only specimens of both colors that were exposed to RH's of 26 and 87% at an elevated temperature of 41°C for eight weeks. Elevated temperatures and humidity extremes are important since the flight hardware is processed in Utah but used in Florida. Pronounced "curling" was observed in the white topcoat/primer TMA specimens exposed to 41°C/87% RH, making film tension tests very difficult. The TMA film tension tests for the eight-week accelerated aging were recently completed, and preliminary data is

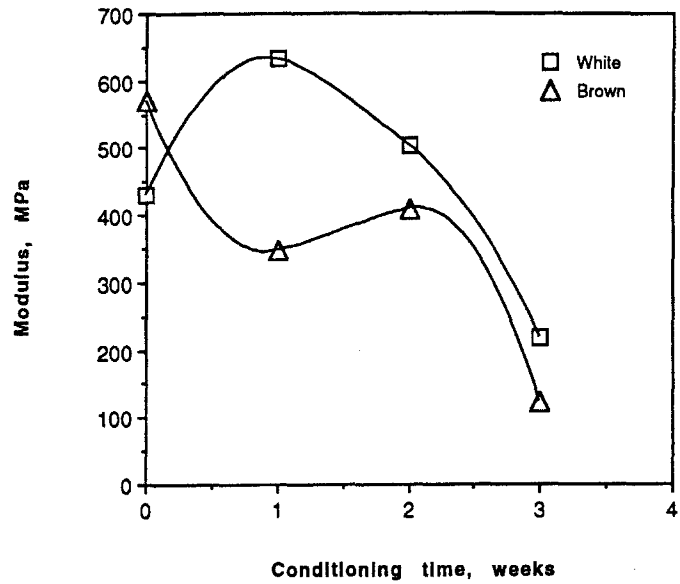

Fig. 4 TMA moduli at 40°C of white and brown topcoat/primer samples exposed to 41°C/105°F and 26% for 3 weeks

shown in Fig. 4. This is a plot of modulus at 40°C *vs.* conditioning time at 41°C and 26% RH. For both the white and brown paints, the modulus increases to a maximum at 1–2 weeks, then rapidly decreases at 3 weeks. Similar trends were observed by TC/W in tensile adhesion data on white and brown topcoat panels exposed to temperatures of 21–60°C (70–140°F) and RH's of 30 and 85% for four weeks.

Summary and conclusions

From TMA film tension data obtained at NASA/MSFC, the vacuum bag material associated with the RSRM "brown paint" anomaly had a lower modulus *vs.* temperature curve than for previously used RSRM bagging materials. The more pliable bagging material would help to explain its permeability to sulfur at elevated temperatures. For paint panels exposed to ambient laboratory conditions, TMA data showed that the brown/white ratios of moduli were about 2/1 and 4/1 for topcoat/primer and topcoat only samples, respectively, from 25 to 55°C. This data is in harmony with microhardness testing on brown and white paint by TC/W. The TMA moduli of brown and white topcoat/primer samples went through a maximum at 1–2 weeks of eight-week conditioning time at 41°C and 26% RH (accelerated aging). Based on TC/W and NASA/MSFC data, the brown paint on the RSRM forward segment was abraded/reapplied in critical bonding regions, with simple encapsulation of the brown paint by a cosmetic white topcoat in case acreage regions.