Special Report No. 3

DEVELOPMENT OF MATERIAL SPECIFICATIONS AND QUALIFICATIONS OF POLYMERIC MATERIALS FOR THE JPL SPACECRAFT MATERIALS GUIDEBOOK III. POLYFLUOROCARBON FILMS

Prepared for:

JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

JPL CONTRACT NO. 950745 UNDER
NASA CONTRACT NO. NAS7-100

JPL COGNIZANT ENGINEER: HUGH MAXWELL

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SUMMARY

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Preliminary outgassing studies were performed on selected polyfluorocarbon films. Five types of film, four of the Tedlar* polyvinyl fluoride films, and one Teflon FEP*, were heated to 150°C and 5 x 10^{-6} mm Hg for over 200 hours. Weight losses for all materials tested were very low, ranging from zero to about 0.5%. Duplicate test specimens of Teflon FEP, differing only in size, were also tested in order to estimate the effect of sample size on weight losses, but no clear relationship was found.

No condensable oils were evolved from the test specimens. All Tedlar samples underwent very slight darkening during thermal vacuum treatment, and an ultraviolet-visible spectrum was run on one of the specimens; the Teflon FEP samples were unchanged.

In view of their low weight losses and the absence of condensable volatiles, all these materials seem suitable for spacecraft applications.

*Trademark for E.I. duPont de Nemours polyfluorocarbon films.

INTRODUCTION

The over-all objective of this program is to provide assistance to the JPL staff members in the development of specifications and procedures for polymeric spacecraft materials. This includes definitions of properties, tests, and environments which are sensitive and meaningful, and collection of pertinent property, environmental, and materials data for use in specifications. Of special importance to this program are the outgassing characteristics of various polymeric materials under thermal vacuum conditions.

At the request of JPL cognizant engineers the first two classes of materials examined were epoxide adhesives and RTV silicone rubbers, and data for these have been reported.[1,2] The third class of materials selected by JPL cognizant engineers were polyfluorocarbons, specifically Tedlar and FEP Teflon films. Samples were cut from the films as received from the manufacturer, and their weight loss characteristics at 150°C and 10^{-6} mm Hg determined. This temperature (150°C) approximates the temperature currently recommended for the sterilization of spacecraft.

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[1] Development of Material Specification and Qualifications of Polymeric Materials for the JPL Spacecraft Materials Guidebook, Special Report No. I. Epoxide Adhesives

[2] Ibid., Special Report No. II. RTV Silicone Rubbers

EXPERIMENTAL

Materials

Samples of Tedlar (polyvinyl fluoride) and Teflon FEP (copolymers of tetrafluoro ethylene and hexafluoropropylene) film were obtained from E.I du Pont de Nemours. Some properties of the various films as well as sample weights and areas are summarized in Table I. The films were tested as received from the manufacturer; no pretreatment or curing were required.

Techniques

Preparation of Test Samples

Test samples of Tedlar and Teflon FEP films were cut to the desired size from sheets of film supplied by the manufacturer. Samples of Tedlar were cut into rectangles 3 x 10 cm; this sample size could be accommodated by the resin pots without folding or curling the films. Because of the scatter of points observed in the testing of the Tedlar samples, the Teflon FEP samples were cut somewhat larger (6 x 22 cm and 3 x 22 cm) in an attempt to improve the accuracy of the weight loss determinations. These samples were rolled before placing in the resin pots. All samples were dusted lightly with a dry tissue before testing to remove any dust or foreign matter from the film surface.

The vacuum system (Fig. 1) which utilizes a mechanical roughing pump (capacity, 140 liters per minute) and a mercury diffusion pump, can achieve routine pressures of 1-5 x 10^{-6} mm Hg. Pressures were measured with an ionization gauge (Consolidated Vacuum Corp.) calibrated for pressures from 0.025 mm to 10^{-7} mm Hg. Test specimens were placed in modified resin kettles (Fig. 2) which were heated in oil baths. These consisted of stainless steel beakers filled with Dow silicone oil No. 550 and heated by resin kettle heating mantles. The bath temperatures were controlled by Thermistemp temperature controllers (Yellow Springs Instrument Co., Model 63RA). The power to the heating mantles was

supplied by a variable autotransformer. This arrangement maintained the oil baths at ± 2° of the desired temperature. In general the bath temperatures were held about five degrees higher to maintain the desired sample temperature. The temperature of the oil baths was measured directly by a mercury thermometer suspended in the bath; the temperature inside the resin pot was determined from a thermocouple wire inserted into the thermocouple tube which extended into the resin pot. Temperature measurements were made using a Leeds and Northrup Model 8692 potentiometer reading directly in degrees centigrade. (Measurements were accurate to approximately ± 0.5°C.) The resin pot led directly to a liquid nitrogen trap which could be isolated from the rest of the system and its contents transferred into a sample bulb suitable for subsequent g.l.c., infrared, or mass spectrometric analysis.

The test specimens were periodically removed from the system and weighed on a Mettler "H" balance, accurate to ± 0.05 mg. Although continuous weighing under vacuum is recognized as a superior method, the present system will accommodate four different samples at one time and permits a rapid screening of materials as requested by JPL.

Thermal Vacuum Testing Procedure

The samples were tested at 150°C and approximately 5 x 10^{-6} mm Hg for total exposures of 150-200 hours. At approximately 24-hour intervals, they were removed for weighing. The temperature of the oil bath and of the interior of the resin pot, as well as the pressure of the system, were recorded at this time. Samples were removed from the resin pots with forceps, allowed to cool, weighed to the nearest 0.01 mg, and returned to the system, which was immediately re-evacuated and the test continued.

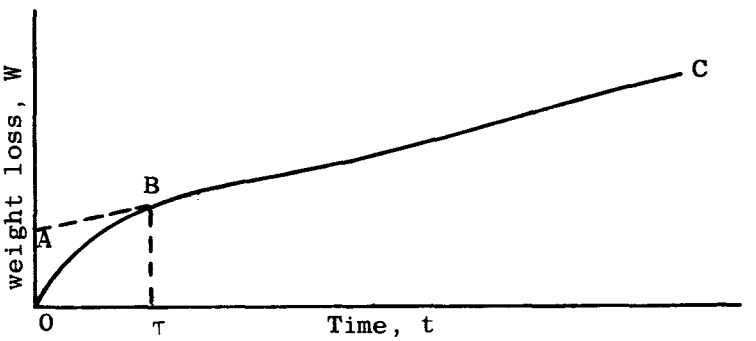
The following raw data were recorded for each test: (1) initial weight and dimensions of the test specimens; (2) weight of the test specimens to the nearest 0.01 mg at 24-hour intervals; (3) temperature of the system; (4) changes in color or other physical properties of the sample; and (5) observations relating to outgassed materials, such as condensable oils on the inside of the head of the resin pot, above the

level of heating.

Ultraviolet spectra of the films were obtained on a Cary Model 14 spectrophotometer.

RESULTS

A plot of material loss versus time is generally of the form:



Steady State is represented by the linear portion (BC) of the curve

Initial Weight Loss is the zero-time intercept of the linear portion of the weight loss curve (A).

Time until Steady State is the time required before the weight loss becomes linear (τ).

Steady State Loss Rate is given by the slope of the linear portion of the weight loss curve ($\Delta W/\Delta T$).

All these parameters are estimated graphically.

Data are reported in two sets of units; in percent of total sample weight, and in absolute weight loss per unit area of exposed surface ($g\ cm^{-2}$).

Figures 3 and 4 show the outgassing curves of the polyfluorocarbon materials tested at 150°C and 10^{-6} mm Hg for 216 hours. The scattering of points is due primarily to the small sample sizes and correspondingly small weight losses. It is believed that a large percentage of the total weight loss is due to desorption of surface moisture and gases, and that some of these readsorb onto the materials while weighing in air.

Continuous weighing under vacuum would, of course, be a vastly superior method for this type of sample.

The most striking feature of the weight loss curves is the difference between the filled (pigmented) materials, TD 30/A and TD 30/B, and the unfilled transparent films. Not only do the filled materials exhibit larger weight losses but in contrast to the others, they exhibit an unequivocal, positive weight loss rate. If the large scatter is taken into account, the curves for TD 30/A and TD 30/B may be considered identical. These two materials differ from each other only in surface preparation, which apparently exerts no effect on the outgassing properties.

It may be seen by a comparison of Figs. 3 and 4, that the thicker films, FEP-a and b (5 mil), show an increase in relative weight loss when replotted in terms of absolute weight loss per unit area. This would indicate that the outgassing is not entirely a surface phenomenon, but involves removal of material from the interior of the polymer sample as well. This is corroborated by the fact that after the treated test specimens had been exposed to air for over two weeks they regained but little of the weight lost under thermal vacuum treatment.

The Tedlar test specimens all underwent a color change during thermal vacuum treatment, going from white or water white to a light brown. Figure 5 shows the UV-visible spectrum from 2500 to 6500Å of TD 40/S before and after thermal vacuum treatment. The spectral characteristics of the UV curve remain similar except for an over-all increase in absorbance of the treated film. The much greater increase in the UV region suggests formation of conjugated systems $(-CH=CH-)_n$.

Because of the scattering of data, the method of least squares was applied on the assumption that a steady state was achieved in less than 24 hours. Tables II and III summarize these least squares parameters, the initial weight losses and weight loss rates, the weight loss after 200 hours, and the root mean square deviations for each curve. Weight losses range from 0-0.5% by weight; weight loss rates are taken as zero for all materials except the pigmented Tedlars, 30/A and 30/B, which lose weight at a rate of approximately 0.001% per hour.

Table I

DU PONT TEDLAR AND TEFLON FEP FILMS

Material	Sample No.	Film Code	Film Type	Surface Characteristics	Color	Thickness	Area cm^2	Weight g
Tedlar[a]	TD 40/S	200 SG 40 TR	low shrinkage	both sides heat sealable	trans.	2 mil	60.0	0.26467
	TD 30/A	200 AG 30 WH	med tensile strength	one side adherable	white	2 mil	59.4	0.23683
	TD 30/B	200 BG 30 WH	med tensile strength	both sides adherable	white	2 mil	60.0	0.25386
	TD 20/A	50 AG 20 TR	high tensile strength	one side adherable	trans.	0.5 mil	55.6	0.04744
Teflon FEP[b]	FEP-a	500 A FEP			trans.	5 mil	260	3.37703
	FEP-b	500 A FEP			trans.	5 mil	130	1.67497

[a] polyvinyl fluoride films

[b] copolymers of tetrafluorethylene and hexafluoropropylene

Table II

OUTGASSING CHARACTERISTICS OF TEDLAR AND TEFLON FEP FILMS AT 150°C and 10^{-6} mm Hg (Weight Loss Data in Percent)

Material	Sample	Initial Wt. Loss, %	Wt. Loss Rate %/100 hrs	% Wt. Loss after 200 hrs	rms Deviation %
Tedlar	TD 40/S	0.14	0	0.14	0.02
	TD 30/A	0.39	0.075	0.54	0.04
	TD 30/B	0.35	0.08	0.50	0.03
	TD 20/A	0-.05	---	0-.05	--
Teflon FEP	a	0.084	< 0	0.075	0.013
	b	0.003	0.02	0.05	0.008

Table III

OUTGASSING CHARACTERISTICS OF TEDLAR AND TEFLON FEP FILMS AT 150°C and 10^{-6} mm Hg (Weight Loss Data in g cm^{-2})

Material	Sample	Initial Wt. Loss g cm^{-2} hr^{-1}	Wt. Loss Rate g cm^{-2} hr^{-1} x 10^{-6}	Wt. Loss after 200 hrs	rms Deviation g cm^{-2} hr^{-1}
Tedlar	TD 40/S	.062	0	.062	.009
	TD 30/A	.156	0.030	.215	.016
	TD 30/B	.148	0.034	.216	.013
	TD 20/A	0-.09	---	0-.09	--
Teflon FEP	a	.109	< 0	.101	.017
	b	.004	.030	.064	.010

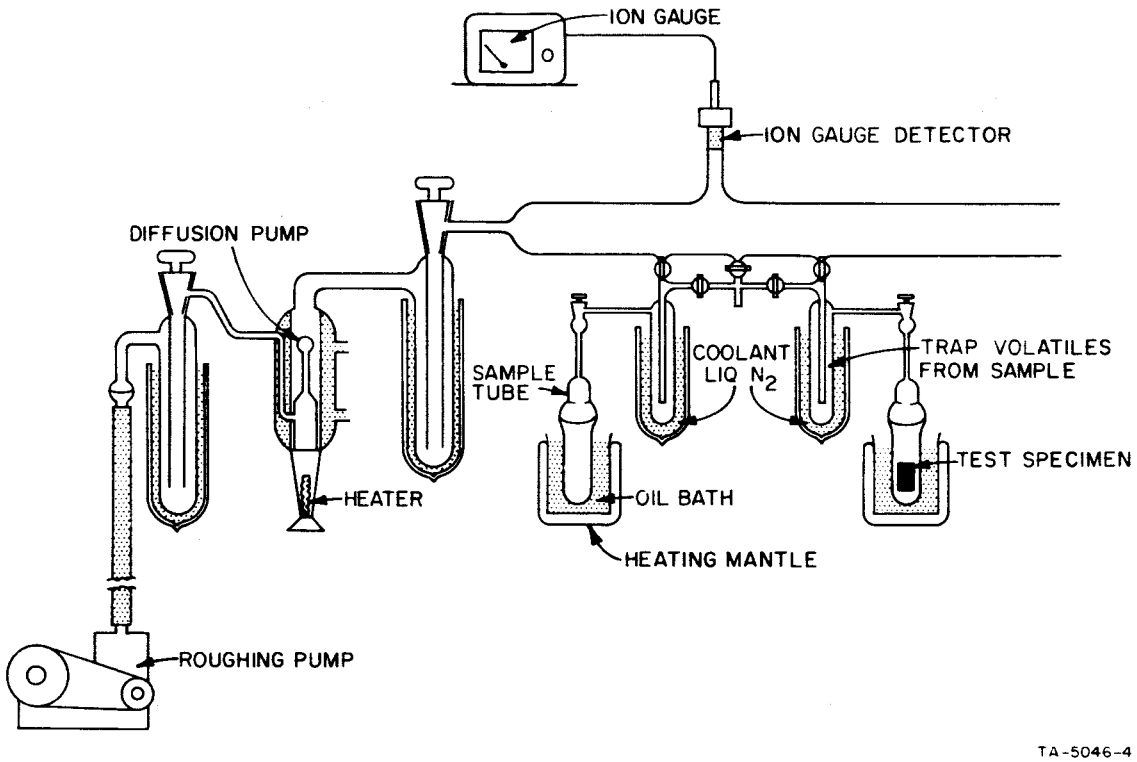


FIG. 1 COMPLETE VACUUM APPARATUS FOR THERMAL VACUUM TREATMENT

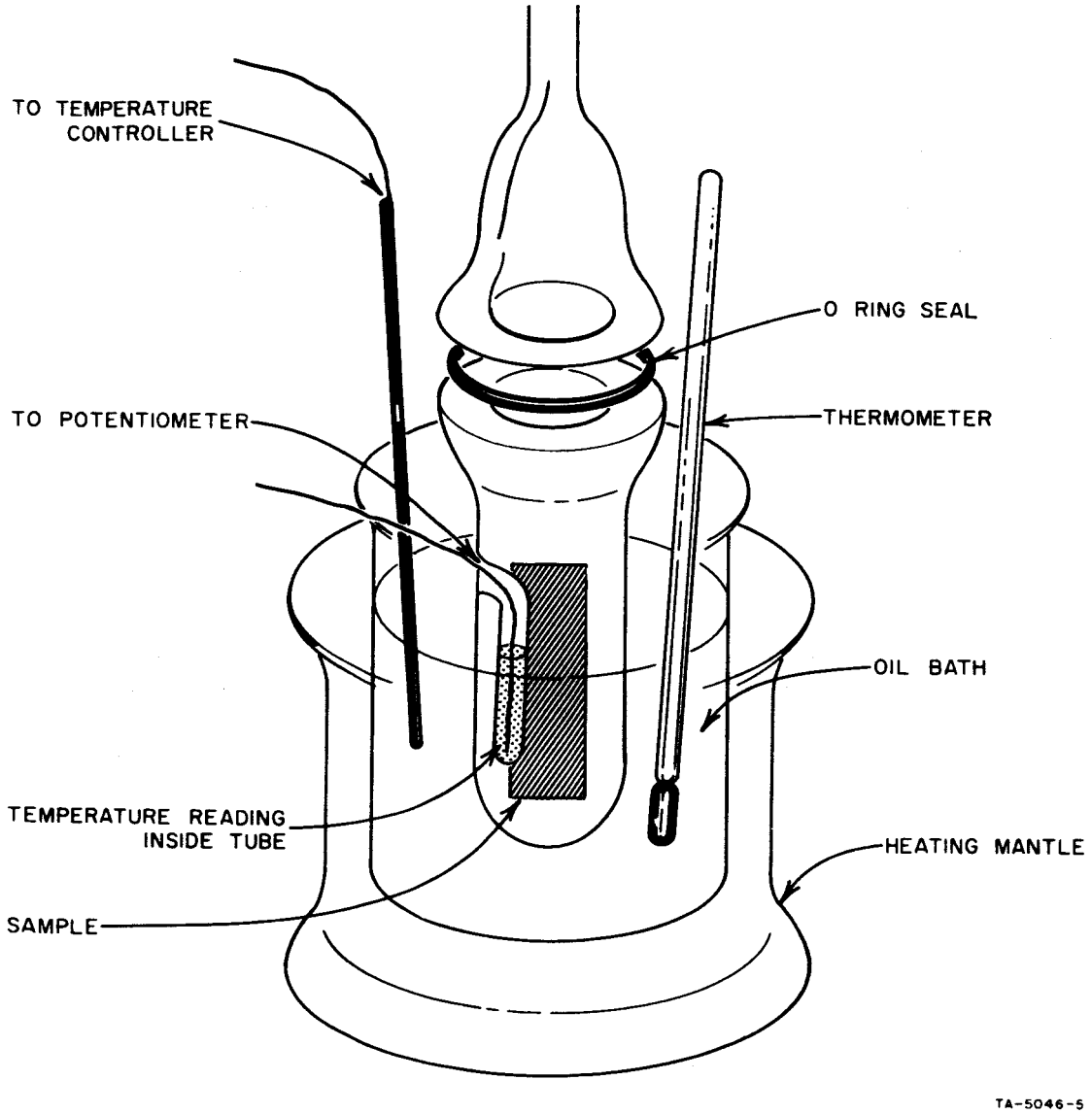


FIG. 2 DETAILED DRAWING OF SAMPLE CELL ASSEMBLY

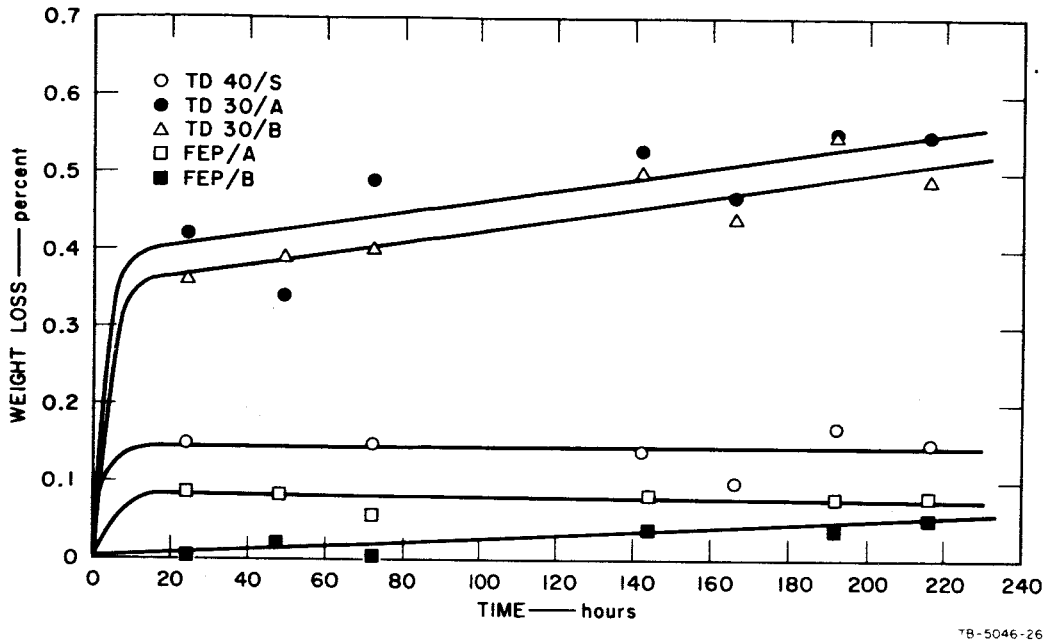


FIG. 3 PERCENT WEIGHT LOSS OF TEDLAR AND TEFLON FEP FILMS AT 150°C AND 5×10^{-6} mm Hg

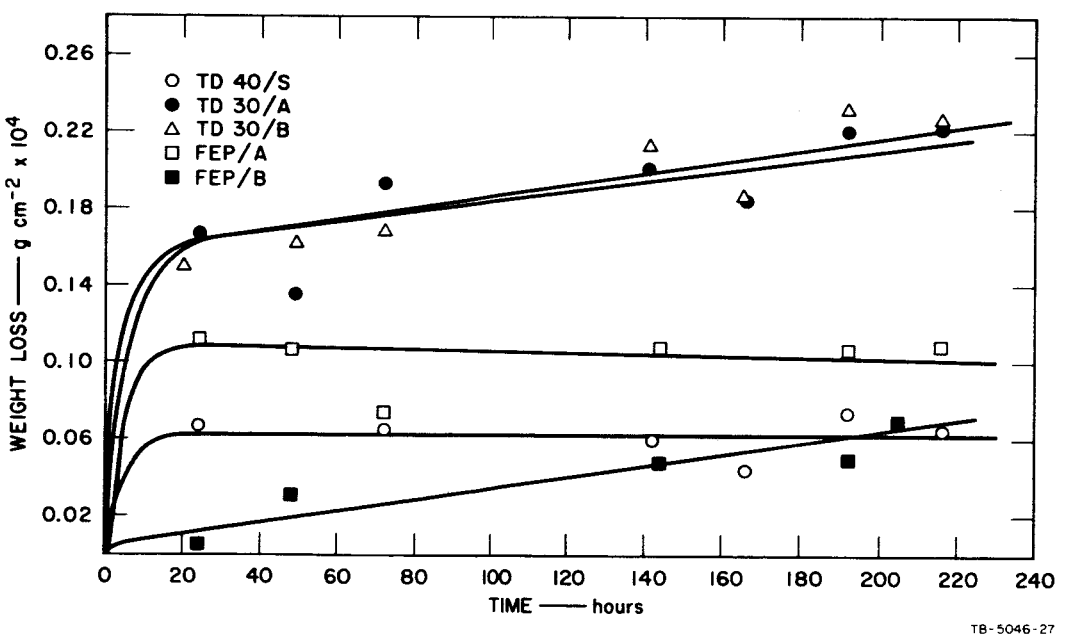


FIG. 4 WEIGHT LOSS PER UNIT SURFACE AREA OF TEDLAR AND TEFLON FEP FILMS AT 150°C AND 5×10^{-6} mm Hg

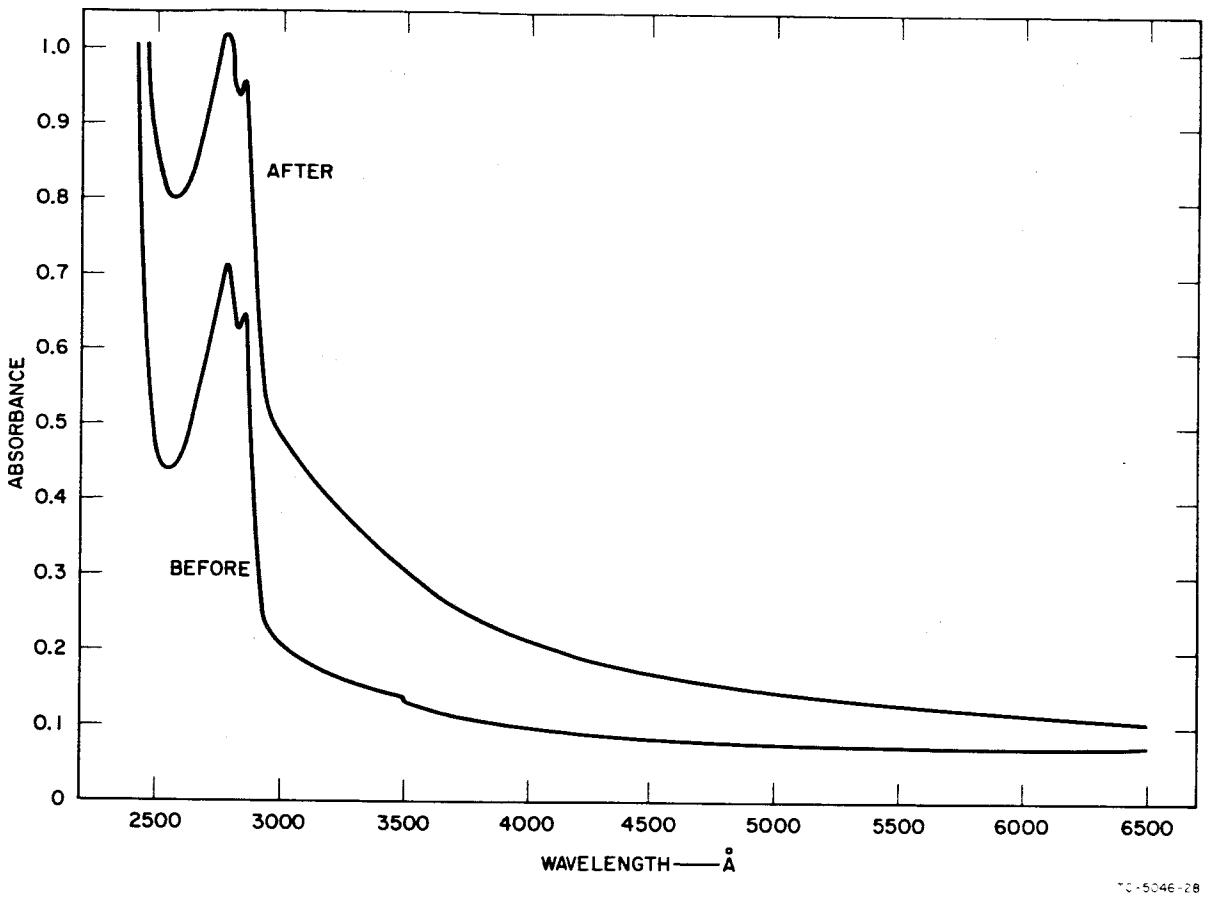


FIG. 5 UV-VISIBLE SPECTRUM OF TEDLAR 40/s BEFORE AND AFTER THERMAL VACUUM TREATMENT

DISCUSSION

A vast amount of literature exists on the behavior of Teflon (polytetrafluorethylene) in simulated space environments.* Jolley and Reed[3] have reviewed over one hundred references on this subject alone, and numerous survey reports on the properties of TFE plastics have been published. Madorsky, et al[4] have examined the thermal degradation of this material, as well as several other fluorinated polymers, in considerable detail. In general, however, less information is available on the hydrofluorinated materials such as Tedlar, [poly(vinyl fluoride)].

In considering the chemistry of these materials it is obvious that polymer degradation would not be expected to be a significant factor, especially in the case of Teflon FEP. This is consistent with the observation that the weight loss of this material at 150°C is indeed very low. It is interesting to note that the weight loss for sample FEP-a, 0.08% after 100 hours, is exactly that observed by Jolley and Reed. This agreement may however be fortuitous, since Jolley and Reed do not supply the dimensions of their test sample.

Since Teflon FEP contains no additives, and since degradation will not occur to any extent at 150°C, it is reasonable to assume that the samll weight loss observed is due primarily to desorption of surface contaminants such as water and carbon dioxide. This conclusion is not entirely consistent with data obtained for two different sample sizes of the same polymer which when reduced to percent or g/cm^2 should exhibit

*Teflon has been found to be heat stable up to 450°C under vacuum. FEP, which is also totally fluorinated, and differs only by the presence of CF_3 side chain on the polymer backbone, would be expected to be similar to Teflon. The substitution of one or more hydrogen atoms for fluorine, however, alters the polymer considerably. For example, polyvinyl fluoride's weight loss of 240°C is similar to that of Teflon at 380°C.

[3]C. E. Jolley and J. C. Reed, Space/Aeronautics, February 1963, p. 105

[4]S. L. Madorsky, V. E. Hart, S. Straus, and V. A. Sedlak, J. Res. Nat'l. Bur. Std., 51, 327-333 (1953).

identical weight losses. The relatively large discrepancy of about 50% is at the present time not clear, but could be due to experimental error. (Tables II, III.)

The samples of Tedlar [poly(vinyl fluoride)] behaved similarly to those of FEP. It was found, however, that the pigmented samples (30/A and 30/B) exhibited much higher weight losses than the transparent Tedlar films. These pigmented Tedlar films also exhibited finite rates of weight loss; this may indicate that the pigment employed is somewhat volatile or contains volatile contaminants. All the Tedlar films tested exhibited some discoloration. This darkening in color has been observed in conjunction with the degradation of poly(vinyl fluoride) and is believed to be due to the formation of conjugated unsaturation in the polymer as a result of the elimination of HF. The slight discoloration observed is, however, of little consequence. As in the case of poly(vinyl chloride), extremely large color changes may take place in the material without any structural changes being observable in the infrared spectra; i.e., degraded material constitutes less than about 1% of total sample.

CONCLUSIONS

It has been found that all the polyfluorocarbon films tested in this study have very low weight losses--all well below 1%--and therefore appear quite suitable for spacecraft use. In view of the comparatively large weight losses of the pigmented Tedlar films (0.5% as compared with approximately 0.1% for the unfilled materials) it would be of interest to investigate the possible use of a new, less volatile pigment. The slight darkening of the Tedlar specimens at 150°C and 5×10^{-6} mm Hg is not considered an indication of serious degradation.