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Spectrometers Results of Material Exposure and Degradation Experiment Onboard International Space Station

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Material Exposure and Degradation Experiment is an active material experiment exposed to the low-Earth-orbit environment for 18 months onboard ISS/Columbus. This paper focuses on the results of Spectrometer experiment, one of the seven subunits of MEDET. The purpose of this experiment is to measure in real time thermooptical properties of a large set of materials designed for space applications (20 different materials). Some of these materials have been developed for atomic oxygen-resistant protection for low-Earth-orbit spacecraft applications. The evolution of their thermooptical properties on the International Space Station orbit allows for monitoring the degradation of materials mainly due to ultraviolet and atomic oxygen before recovery phenomena take place at the time the experiment returns into the atmosphere. Ultraviolet-visible transmission spectra from preliminary flight data highlight the two degradation phenomena expected for such a mission, namely: yellowing for atomic oxygen protected polymeric films and silicone resins due to ultraviolet exposure, and the decrease of thicknesses for other samples like polymeric films due to atomic oxygen erosion.

I. Introduction

MEDET is an active material experiment exposed to the low-Earth-orbit (LEO) environment during 18 months onboard EuTEF/Columbus, from February 2008 to September 2009. It is a fruitful collaboration between ONERA, ESA, Centre National d'Etudes Spatiales (CNES), and the University of Southampton. It combines seven subexperiments devoted to the measure of the radiative space environment in LEO and its associated effects on materials. It allows for real-time characterization of the International Space Station (ISS) local environment and materials degradation. Usually, most studies about the effect of LEO environment on spacecraft materials are based on laboratory or postflight investigations. The experiment is a mean to validate the use of a diverse collection of materials potential candidates for LEO applications. The degradation of materials in LEO environment is difficult to know precisely because when materials are in interaction with oxygen, at the time of the experiment return, recovery phenomena occur and anneal degradations. The active experiment MEDET allows for characterizing the in situ material degradations mainly due to ultraviolet (UV) and atomic oxygen (AO). The synergetic effects of UV and AO degradations will be evaluated for each material. MEDET experiments (and then Spectrometer) are mostly oriented in RAM on the ISS orbit (92% of mission time in RAM).

The paper focuses on the results of Spectrometer experiment, which surveys the thermooptical properties of 20 different materials normally used for space applications. Samples included different polymeric films with and without atomic oxygen protection coating, quartz with and without thermal control coating, and solar cell cover glass adhesives. Data collected by Spectrometer experiment are UV-visible and Visible-Infrared (V-IR) transmission spectra.

It is well known that the interaction of AO with spacecraft surfaces results in mass loss or gain, change in surface morphology and optical, mechanical and thermal properties [1–5], hence the interest of this experiment. Kapton film is one of the most studied materials and sensitive to AO degradation [1–5]. Kapton is often considered as a reference to determine the average atomic oxygen fluence. This large amount of data from space experiments will be helpful to explain our results.

The preliminary analyses of UV-visible spectra of some samples will be presented in this paper. This work was focused on the change of UV-visible properties of materials to highlight degradation phenomena such as yellowing or erosion. Indeed, the shift of UV cut-off and the change of transmission intensity have been particularly studied to understand the material degradation. IR results are being analyzed and are not reported in this paper.

II. Experimental Data

A. Spectrometer Description

The optical spectral transmission of the samples are measured by a system composed of quartz optical fibres, two miniature spectrometer modules (to cover the solar spectrum from 200 to 1000 nm) and two illumination sensors (IS). The materials samples are placed on a rotating wheel, containing 24 apertures (Fig. 1) and the sun is used as the light source. Therefore, measurements are only allowed when the light detected by the illumination sensors is in a $\pm 40°$ acceptance angle (see Fig. 2). An encoder system, consisting of photodiodes (behind the wheel) and holes pattern onto the wheel, is used to identify the position of the wheel with respect to the fibre optics at any given instant. Sun light passing through the sample is collected by a quartz diffuser to illuminate as homogeneously as possible a fibre optics strand. Half of the collected light is transmitted by UV fibers to a UV-visible spectrometer sensitive to the 200–700 nm range and the second half to a visible-IR spectrometer sensitive in the 400–1000 nm range.

Each miniature spectrometer module consists of a grating, optics, and a charge-coupled device (CCD) detector. These are all rigidly housed within the same case. The module is based on a standard laboratory device (Zeiss MMS) which has been adapted for this flight mission. However, to be operated safely on MEDET, which is an external payload, the miniature spectrometer modules are mounted in a sealed cylinder. For redundancy, two sets of these cylinders (with two spectrometers in each) are mounted behind the filter wheel. Both

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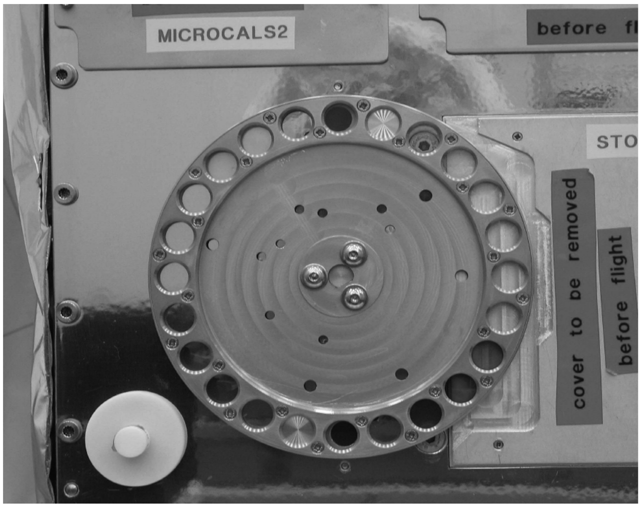

Fig. 1 Flight wheel sample.

are operating simultaneously allowing each sample to be measured twice at each wheel rotation.

Visible-IR and UV-visible spectrometers for each material are acquired once or twice per day (depending on illumination conditions) since MEDET commissioning (i.e., 18 months in LEO exposure), except for some small data gaps due to power outages at MEDET/European Technology Exposure Facility (EUTUF) levels.

B. Samples

Samples are different polymeric films with and without atomic oxygen protective coating, quartz with and without thermal control coating, and solar cell cover glass adhesives. The list of flight samples is listed in Table 1.

In this paper, focus is placed on the UV-visible analyses of some of these samples as disclosed below sorted by material type (Table 2).

C. AO Erosion Calculation

Atomic oxygen fluence has been measured onboard MEDET with carbon coated quartz crystal microbalances (QCM) sensors [6] for a short period of time (16 days) at the beginning of the mission and has been estimated to $3.11{*}10^{21}$ atom/cm^2 for the entire mission (Ram AO-facing tray for 18 months). ONERA has developed a program able to determine the AO flux per day based on the ISS altitude, solar activity, and MEDET exposure (AO or non-AO-facing tray). ISS position data have been given by NASA and solar activity data come

Table 1 Selection of flight samples

Use	Material
Flexible and rigid thermal control coatings	Ex : Flexible solar reflector, rigid solar reflector
Reference for coatings	Quartz
Solar cell cover glass adhesives	Ex : RTV-S690 and S695, DC-93 500
Thermal control foils	Ex : Upilex® S, Upilex® RN, Kapton® HN
Atomic oxygen protection coatings	Kapton® HN with different kinds of Mapatox coatings
Multilayer polymeric film for inflatable structures	Ex : KF01C01
Polymeric film for inflatable structures	PEN

Table 2 Selection of flight samples studied

Material nature	thickness	Sample type
Polyimide (Kapton® HN)	75 μm	Film
Polyimide with AO protection (Kapton® HN + Mapatox K)	95 μm	Film
Polyimide (Upilex® S)	25 μm	Film
Quartz	2 mm	Quartz
PEN	2 μm + 2 mm	2 μm film between two 1 mm quartz
Thermal control coating on quartz (silicone resin based on polydimethylsiloxane)	2.12 mm	2 mm quartz with coating

from the geostationary operational environmental satellites American satellite (Geostationary Operational Environmental Satellites). It is interesting to notice here that the solar activity is at minimum for the entire mission.

ONERA program calculates AO flux and fluence received by the MEDET experiments in RAM position and estimated to $2.29{*}10^{21}$ atom/cm^2 the fluence for the entire mission. The preliminary results obtained by Tighe et al. [6] with the carbon coated QCM sensors, enabled to calculate an AO fluence in agreement with our result. Erosion yield data given by De Groh et al. [3] for a large amount of materials allows for determining the thickness eroded by AO for certain materials as Kapton HN, Upilex S. For example, according to ONERA calculation, Kapton HN eroded thickness is 69 μm for the MEDET mission (the erosion yield of Kapton HN is $3{*}10^{-24}$ cm^3/atom [3]).

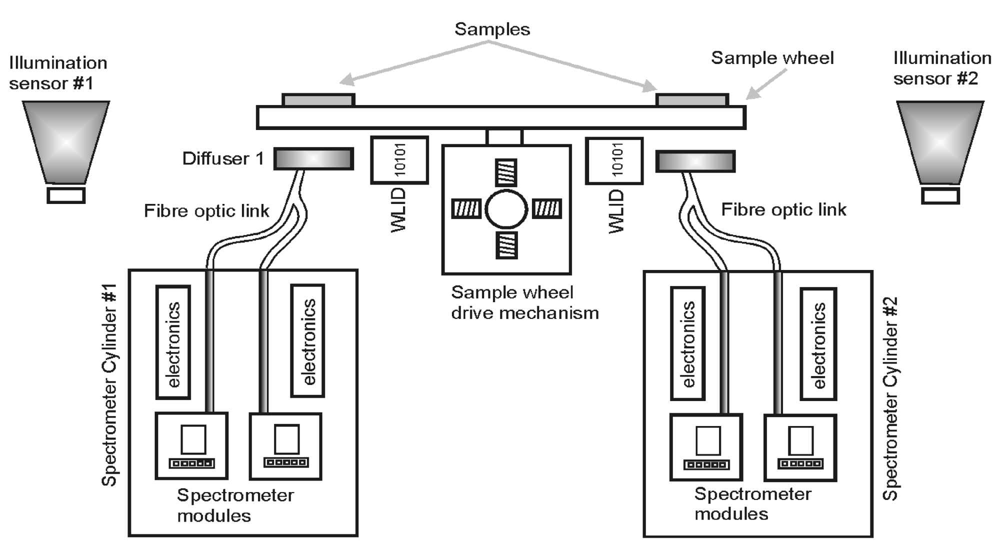

Fig. 2 Schematic of spectrometer experiment.

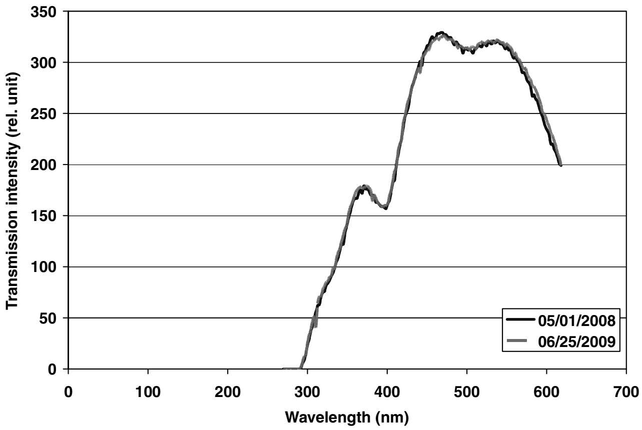

Fig. 3 UV-visible spectra of open position for IS = 8.62 V on 1 May 2008 and 25 June 2009.

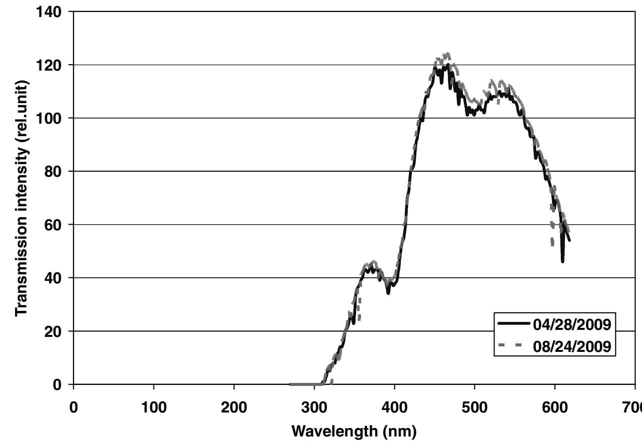

Fig. 4 UV-visible spectra of open position for IS = 9.02 V on 28 April 2009 and 24 August 2009.

D. Spectrometer Record Filtering

Spectrometer experiment has enabled to collect a large amount of raw UV-visible spectra for each material. The first work of the study was to sort data and to find a method to compare and highlight the thermooptical change of materials versus condition exposures.

Spectrometers are not calibrated on a reference sample, and then raw data are obtained and hardly comparable. Two open positions in the wheel have been chosen to be measured as reference (no sample, i.e., measurements at these positions should not evolve with time). Moreover data are collected during 18 months for different illumination conditions and light incidences. The exposure conditions can be directly measured by ISs, situated close to the samples, and then an IS value is attributed to each spectrum. The data sorting has been carried out by acquisition, i.e., analysis of all samples at one date (wheel rotation analysis).

Open position spectra data and IS values are two key parameters to compare materials UV-visible spectra for different periods of acquisitions. Two acquisitions are comparable when IS values are close for a part or all of the samples and when open position spectra are identical (0.5% is the maximum difference defined as the selection between two dates).

Several configurations and periods of acquisition were determined where open position spectra are perfectly identical for a same value of IS, for example the 1 May 2008 and 25 June 2009 records (Fig. 3 and Table 3) or 28 April 2009 and 24 August 2009 acquisitions (Fig. 4 and Table 4). The paper is focused on these two periods. A difference of IS values greater than 0.5% is observed for Upilex® S for these two periods but it is reported here on the shape of UV-visible spectra instead of a real comparison value of UV-visible spectra (Sec. III.C).

The sensitivity of IS varies from 0 to 10 V and has been calibrated in ONERA laboratory. The maximum value corresponds to illumination of one solar constant with normal incidence, simulated by xenon lamp at 1 m.

III. Flight Results and Discussion

For two comparable periods of analyses (1 May 2008 and 25 June 2009, 28 April 2009 and 24 August 2009), the UV-visible spectra for the different samples was studied. UV-visible spectra give information on thermooptical properties of samples enabling to determine yellowing, erosion and contamination degradations. Organic materials in LEO environment mainly suffer from atomic oxygen erosion. The synergetic effects of UV and AO degradations were evaluated for each material.

A. Kapton® HN Film Without AO Protection

Kapton is one of the most studied materials suffering deterioration under the combined effect of AO and UV radiation. The main degradations expected are a decrease of the thickness and the presence of rough eroded surface characterized by a conelike morphology as demonstrated by De Groh for MISSE 2 samples [5]. According to this study, the change of UV-visible spectra during the flight (Figs. 5 and 6) with a shift of UV cut-off toward smaller wavelengths and an increase of the overall transmission intensity reveals the presence of degradation on Kapton HN, which confirms the loss of thickness as expected. At ground, UV-visible properties of Kapton films were measured with different thicknesses and the same results were obtained. However, ground samples did not suffer from AO erosion. With the rough surface, the UV-visible properties are disturbed. A deeper ground study should be conducted to show this notion and confirm the result.

The same response is observed for the two different periods of LEO exposure. So far, the only exploitable data for this sample are the raw flight spectra and are disturbed by the influence of the rough surface. Consequently, the interpretation concerning the kinetic of thickness decrease is still difficult and incomplete.

Referring to the ONERA calculation (Sec. II.C), the current thickness of Kapton HN can be assumed to be around 6 μm at the end of the mission with an AO fluence of $2.29{*}10^{21}$ atom/cm^2. The loss in thickness would be of 69 μm caused by AO erosion in 18 months flight. This result should be checked by postflight analysis. However Dever et al. [2] and De Groh et al. [3] determined the thickness erosion of Kapton HN at 84 μm/year on passive samples on MISSE 2 with an AO fluence of $2.8{*}10^{21}$ atom/cm^2 for 1 yr.

Table 3 IS values in volt for samples studied on 1 May 2008 and 25 June 2009 (10 V corresponds to about 1 solar constant at 1 m)

Sample	IS value for 1 May 2008	IS value for 25 June 2009
Open position	8.63 V	8.62 V
Kapton® HN	8.72 V	8.70 V
Kapton® HN + Mapatox K	8.79 V	8.76 V
Quartz	8.93 V	8.89 V
PEN between 2 quartz	9.09 V	9.11 V
Silicone resin on quartz	9.03 V	9.01 V

Table 4 UV-visible spectra of open position for IS = 9.02 V on 28 April 2009 and 24 August 2009

Sample	IS value for 28 April 2009	IS value for 24 August 2009
Open position	9.01 V	9.03 V
Kapton® HN	8.61 V	8.60 V
Kapton® HN + Mapatox K	8.69 V	8.68 V
Quartz	8.82 V	8.81 V
PEN between 2 quartz	9.03 V	9.03 V
Silicone resin on quartz	8.94 V	8.94 V

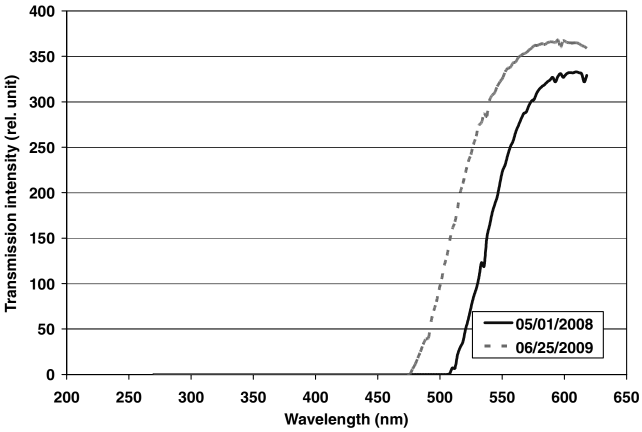

Fig. 5 UV-visible spectra of Kapton HN between 1 May 2008 and 25 June 2009.

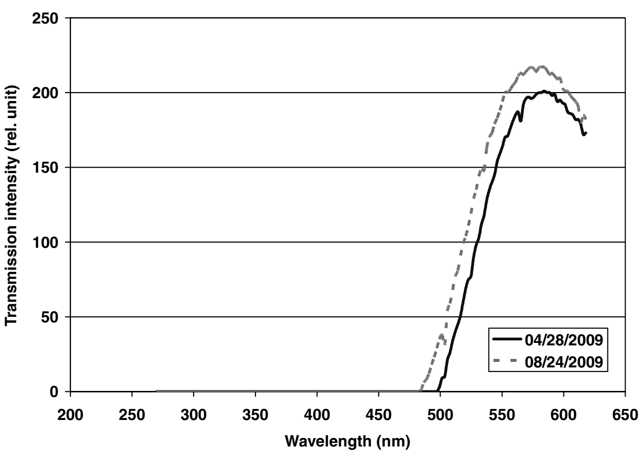

Fig. 6 UV-visible spectra of Kapton HN between 28 April 2009 and 24 August 2009.

B. Kapton® HN Film with AO Protection Mapatox K

Mapatox K is an atomic oxygen resistant coating based on polysiloxane. During a ground study performed by Remaury et al. [7] in an AO simulating chamber (ONERA equipment), this coating appeared as nonsensitive to UV and AO and hence the best protective coating for Kapton. Indeed the coating has shown a good stability of its thermooptical properties. The measure of UV-visible transmission during MEDET mission confirms this ground results and validate the efficiency of Mapatox K as discussed below.

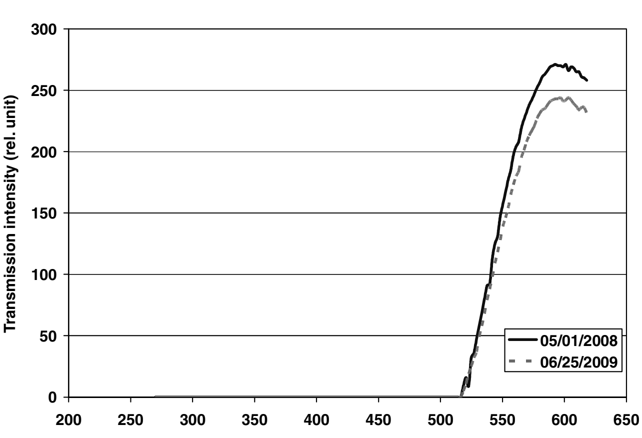

Fig. 7 UV-visible spectra of Kapton HN with Mapatox K between 1 May 2008 and 25 June 2009.

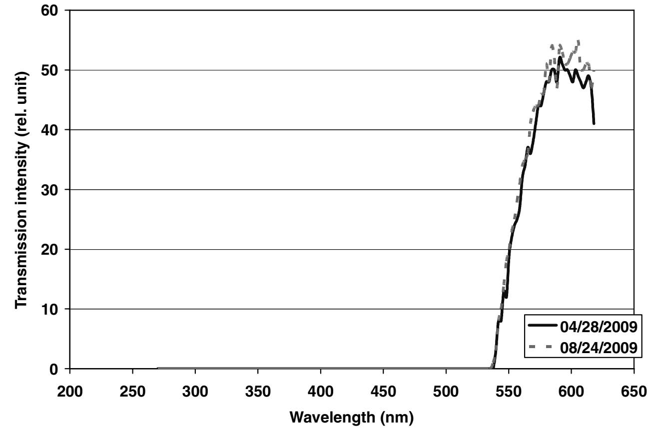

Fig. 8 UV-visible spectra of Kapton HN with Mapatox K between 28 April 2009 and 24 August 2009.

UV-visible spectra of Kapton HN with AO protection are given in Figs. 7 and 8. Kapton HN protected spectra reveals a stability of the UV cut-off compared with unprotected Kapton HN. However, a slight decrease of transmission intensity between the beginning and the end of the mission can be noticed (Fig. 7). It can be explained by the presence of contamination or microcracks at the surface of Mapatox K. The hypotheses will be checked by postflight analysis. Figure 8 confirms the stability of the thermooptical properties of the sample at the end of the mission between April and August 2009. The efficiency of the coating protection is highlighted and confirmed by the analysis.

C. Upilex® S Film Without AO Protection

The Upilex film is the thinner film studied here, 25 μm of thickness. The analysis of UV-visible spectra between the two studied periods reveals a change of the shape of the sample spectra (Fig. 9). The UV-visible curve in June 2009 has the same shape as the open position spectrum. Similarly to Kapton without protection, Upilex S suffers from AO erosion. To date, the Upilex 25 μm sample has been completely eroded by AO.

The Upilex UV-visible curves were investigated in detail to determine the kinetic of the degradation. The spectra used are not fully comparable due to different exposure conditions but they highlight the shape of curves and AO erosion (Fig. 10).

The UV-visible spectra (Fig. 10) show that a pronounced degradation occurred from January 2009 with the distortion of the curve. The spectrum obtained in March corresponds to the open position curve. In 12 months, the erosion of the Upilex sample was complete and so the thickness loss is 25 μm. However, the calculations give a thickness loss of 14 μm for 12 months (erosion yield $9.22^{*}10^{-25}$ $cm^3/atom$, AO fluence $2.29^{*}10^{21}$ $atom/cm^2$ for 18 months). The works of Dever et al. [2] and De Groh et al. [3] confirm this result with a value of 18 μm per year, as well as

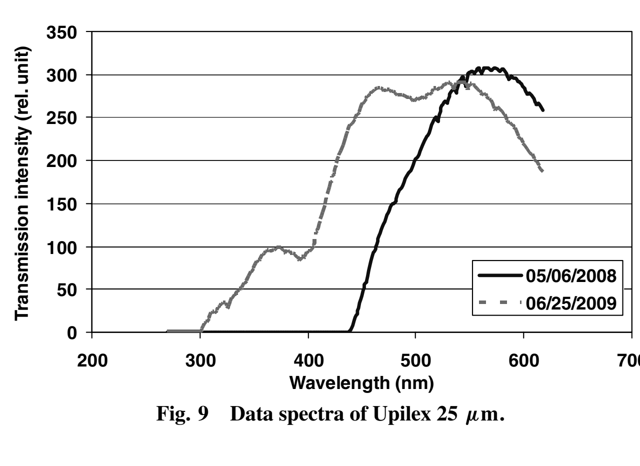

Fig. 9 Data spectra of Upilex 25 μm.

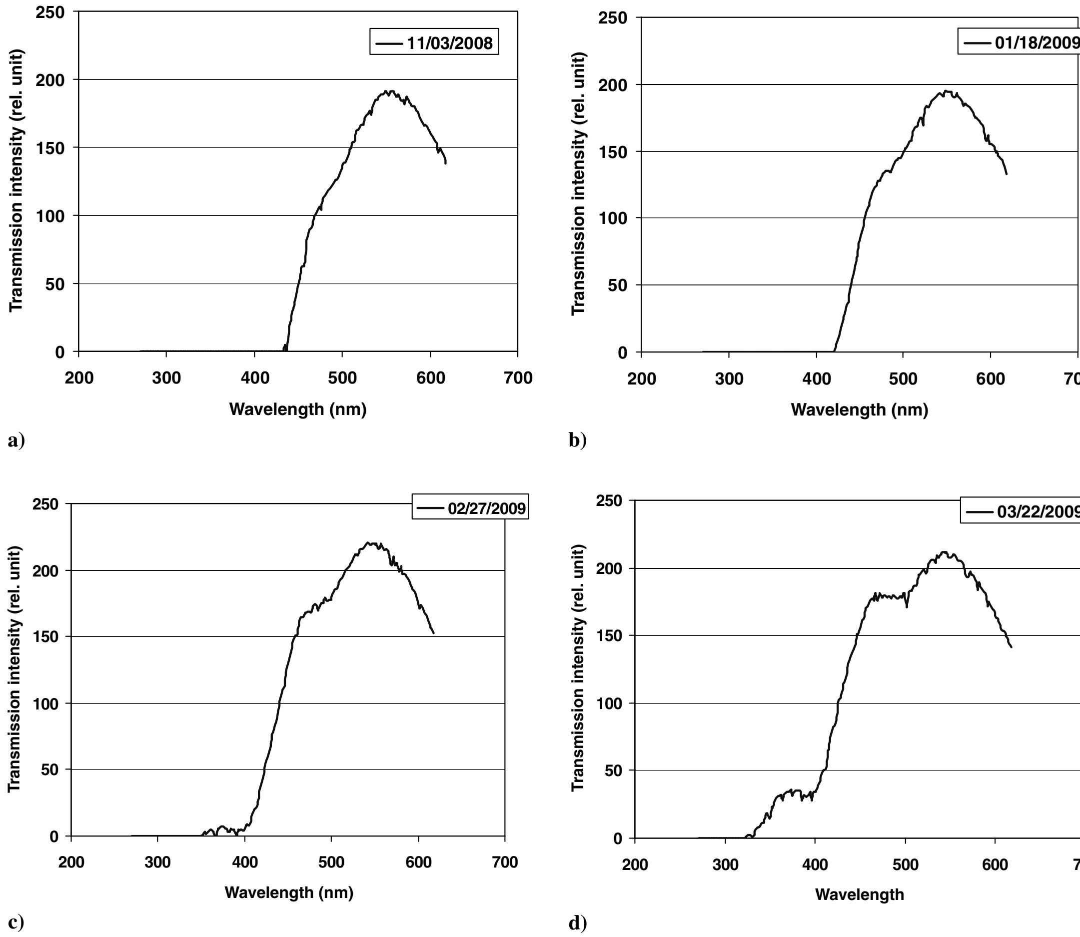

Fig. 10 UV-visible spectra of Upilex 25 μm at different dates: 1) 3 November 2008 (IS = 9.18 V), 2) 18 January 2009 (IS = 9.21 V), 3) 27 February 2009 (IS = 9.18 V), and 4) 22 March 2009 (IS = 9.36 V).

Shimamura [8], who showed that in LEO Upilex thickness loss is around 28 μm/year. It has been shown that the erosion is an inhomogeneous phenomenon [5] which can produce holes in the sample. The thinness of Upilex S and therefore fragility (no substrate) and the possible holes in the material could have enhanced some tearing explaining why a complete erosion of Upilex is observed in 1 yr.

D. Quartz

The stability of uncoated quartz under radiation is well known [1]. The same UV-visible spectra here between the beginning and the end of the mission are expected. However, as shown on Fig. 11, a slight decrease is observed for the spectra amplitude after 13 months exposure. This decrease in transmission intensity of the uncoated quartz could be attributed to contamination.

Figure 12 shows the stability of the thermooptical properties of the quartz at the end of the mission between April and August 2009. At the return of MEDET and the samples, an UV-visible analysis before and after cleaning quartz is planned to confirm our hypothesis.

E. Polyethylene Naphthalate Film Between Two 1mm Quartz

Investigations on a polymer film between two quartz substrates allow for selecting the influence of one parameter namely UV

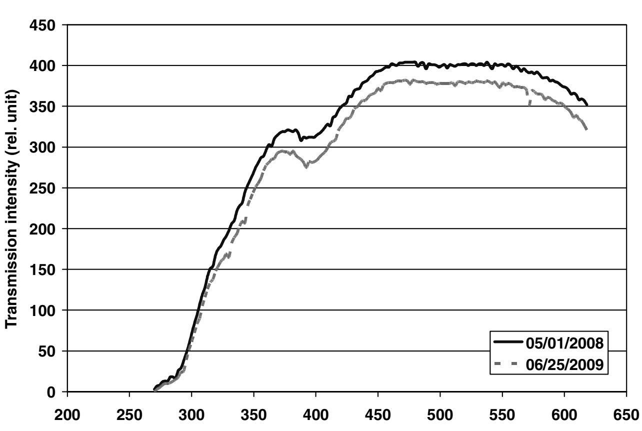

Fig. 11 UV-visible spectra of 2 mm quartz between 1 May 2008 and 25 June 2009.

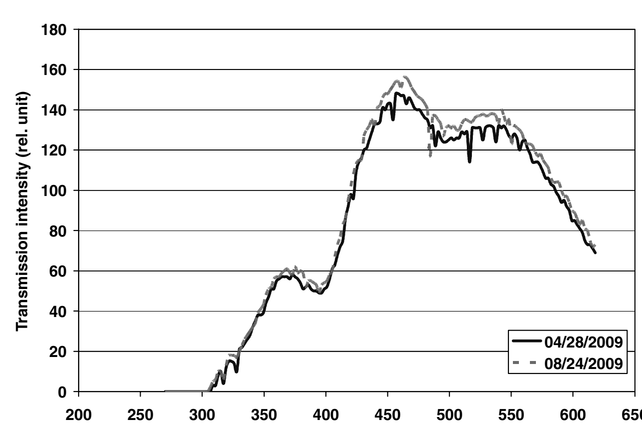

Fig. 12 UV-visible spectra of 2 mm quartz between 28 April 2009 and 24 August 2009.

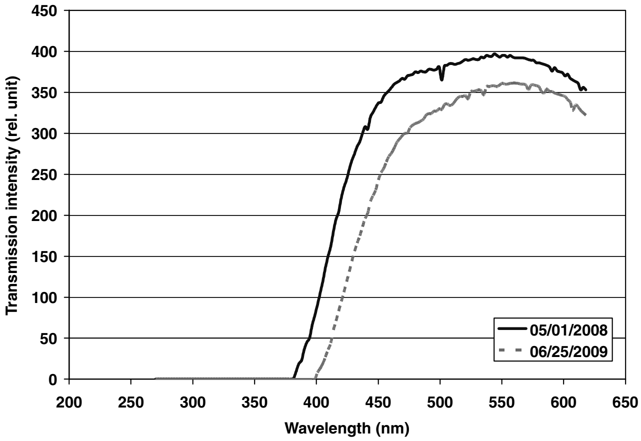

Fig. 13 UV-visible spectra of PEN film between two 1 mm quartz between 1 May 2008 and 25 June 2009.

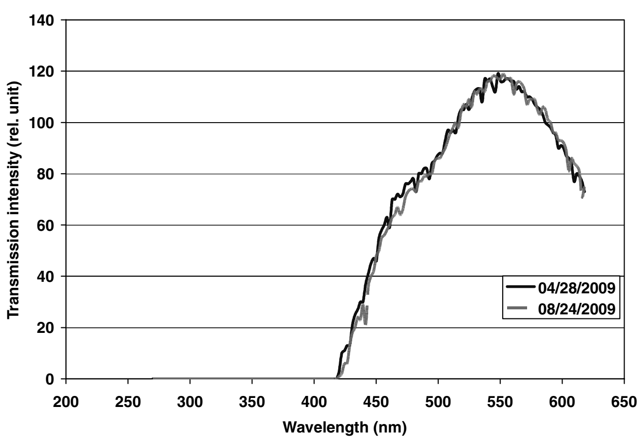

Fig. 14 UV-visible spectra of PEN film between two 1 mm quartz between 28 April 2009 and 24 August 2009.

exposure on the degradation of such a material. Quartz protects polyethylene naphthalate (PEN) against AO erosion and as it has been shown (Sec. III.D) can suffer from a slight contamination.

Figure 13 shows a shift of the UV cut-off toward the higher wavelengths and a decrease of transmission intensity between May 2008 and June 2009. This result is explained by a yellowing of the material under UV exposure and certainly also by the presence of contamination. The absorptance value of the PEN film is now higher than at the beginning of the mission. Further analyses and correlation with ground data are planned to quantify this effect. The film probably exhibits saturations phenomena because UV-visible spectra

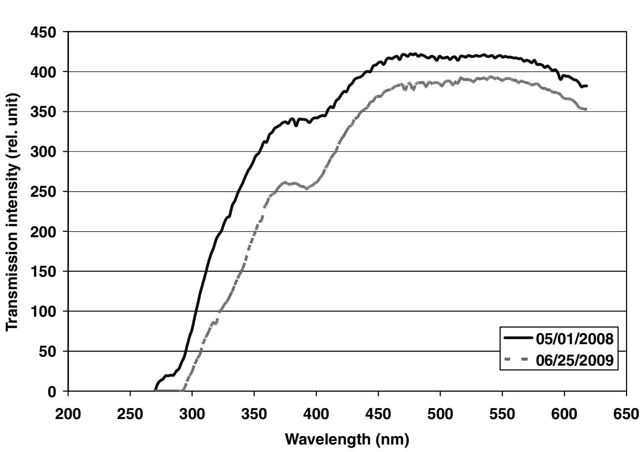

Fig. 15 UV-visible spectra of quartz with silicone resin between 1 May 2008 and 25 June 2009.

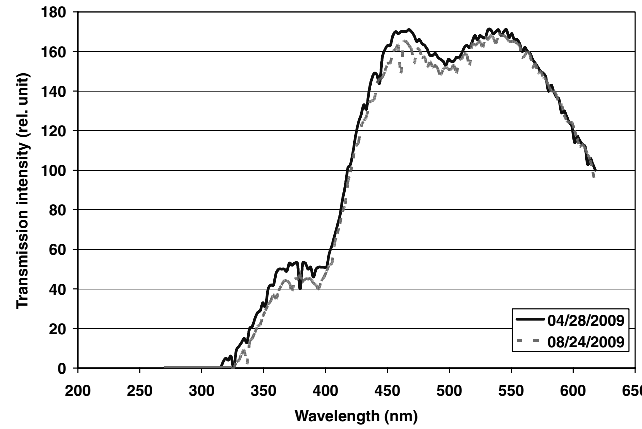

Fig. 16 UV-visible spectra of quartz with silicone resin between 28 April 2009 and 24 August 2009.

stop evolving during the last period of the mission (Fig. 14). The AO protection of the PEN film by the two quartz windows permits to evaluate UV effects on these kinds of materials.

F. Quartz with Silicone Resin

Different thermal control coatings based on silicone resin have been investigated during the mission. Only one result is presented here in Figs. 15 and 16 because similar shape curves are obtained for all of them. Silicone-based paints are generally degraded due to UV exposure and are sensitive to AO erosion.

A shift of UV-visible spectrum toward higher wavelengths and a decrease of transmission intensity are noticed (Figs. 15 and 16). The shift of UV cut-off toward higher wavelengths characterizes a yellowing of the coating and the decrease of transmission intensity is associated to the change of surface state. Indeed in presence of AO, a silicon oxide layer is formed at the silicone-based material surface. The layer is then stable under AO flux but can be degraded by UV exposure (a cracking network certainly appears). The synergy between UV and AO flux can be identified with this sample. The state of surface will be analyzed by postflight analysis.

IV. Conclusions

Spectrometer experiment on MEDET has been a successful experiment for the thermooptical measurements of materials in real-time mission.

QCM experiment and ONERA calculation enabled to determined AO fluence during the mission (18 months), namely between $2^{*}10^{21}$ and $3^{*}10^{21}$ atom/cm. The value is lower than the fluence determined in MISSE 2. This result will be confirmed by the determination of thickness erosion of Kapton HN.

Preliminary UV-visible results presented here show a tendency of samples response in real time for a set of materials in LEO orbit; erosion of polymeric film has been qualified, Mapatox K appeared as an efficient AO protection, thermal coating yellowed.

A deeper study of the UV and IR spectra obtained in flight conditions is necessary to propose a real quantification of the evolution of the degradation for our set of materials (per month for example).

A further accomplishment is the experiments' return to earth and postflight analyses. The materials will be analyzed at ground and laboratory facilities and a direct comparison will be made between the in-orbit results and the ground based results. Furthermore physicochemical analyses are planned to assess in detail the degradation mechanisms.

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