A DETAILED STUDY ON THE THERMAL ENDURANCE OF KAPTON HN™ *1 AND UPILEX S™ *2

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ABSTRACT

Assessing the thermal endurance by isothermal testing in a Thermogravimetric Analyser (TGA) is a time consuming method. A quicker method is to perform kinetic modelling on several decomposition curves. Four temperature scans at different heating rates were recorded with the TGA for two thermal control foils, Kapton HN and Upilex S. Two methods of kinetic modelling were used to calculate the activation energy, i.e. the ASTM E 1641 and the approach of Model Free Kinetics (MFK). The first assumes a constant value for the activation energy whereas the latter calculates it as a function of the conversion. With the activation energy it is possible to make a lifetime prediction that indicates the mass loss that occurs at a certain temperature for a certain duration. The lifetime predictions are used to compare the two materials and also the two modelling methods. The modelling is verified by comparing the results to isothermal TGA tests and thermal ageing of samples in high vacuum chambers at 350 °C for durations up to half a year and in combination with UV irradiation screening tests.

All the performed experiments indicate that Upilex S has a better thermal endurance than Kapton HN. The results of the kinetic modelling are in good agreement with the isothermal experiments in the TGA and in the vacuum facilities. The MFK approach for kinetic modelling was found to be more adequate than the ASTM method.

1. INTRODUCTION

The European Space Agency is currently planning missions to the inner part of the solar system (i.e. Mercury, Venus). A major concern regarding the selection of materials is the behaviour and the stability of external surfaces that will receive heat inputs above 10 kW/m^2. To insulate a spacecraft from the high thermal load, multi-layer insulations (MLI) are used that are composed of materials that have a low solar absorptance and a high thermal emittance. Kapton HN and Upilex S are two polyimide materials that have stable thermo-optical properties and the first is often the baseline for MLI's. With decomposition temperatures well above 400 °C, these polyimides are interesting because of their thermal endurance. The service temperature defines a maximum temperature at which the degradation (of thermo-optical properties) remains within acceptable limits. With the high thermal loads that are expected on the inner solar system planetary missions, these materials will be used on the limits of their service temperature.

The degradation of these materials can be investigated directly by measuring for instance the thermo-optical properties, because these are the relevant properties from an engineering point of view. But also mass loss is a good indication of degradation and decomposition processes. In this paper detailed results of a comparative thermogravimetric analysis (TGA) are presented.

The thermogravimetric analyser is an Ultra Micro Balance in a temperature-controlled furnace that is usually purged with an inert atmosphere like nitrogen. Isothermal tests at the planned service temperature, i.e. 350 °C for the Mercury mission, can indicate the thermal endurance of the sample material at that temperature. With this method it is hard to extrapolate for long durations (years) of thermal ageing or to other temperatures and the balance drift limits the accuracy of the measurements. A faster way to make predictions of the behaviour of a material is to perform kinetic modelling of the decomposition curves of the material. The so-called lifetime predictions of the kinetic model can be verified with isothermal TGA tests. In this paper, experimental TGA results are presented. An introduction to the theory is presented in [1].

*1 *Kapton HN is a trademark of DuPont, USA.*
*2 *Upilex S is a trademark of UBE Industries, Japan.*

The results of the kinetic modelling of the TGA curves can be compared to so-called environmental tests. The mass of samples of both the polyimides is measured with an Ultra Micro Balance before and after environmental exposures. In the High Temperature Exposure System (HITES) the samples are thermally aged at 350°C in a high vacuum chamber. In the Solar UltraViolet facility (SUV) the samples are irradiated with UV light in combination with thermal ageing at 350°C in a high vacuum chamber.

2. TGA TEST RESULTS

2.1. Temperature scans

The kinetic modelling is based on four TGA temperature scans, during which the sample is heated at four different heating rates. This is shown in Fig. 1 and 2. The mass losses of both materials are compared in the lower limit of the decomposition process in Fig. 3.

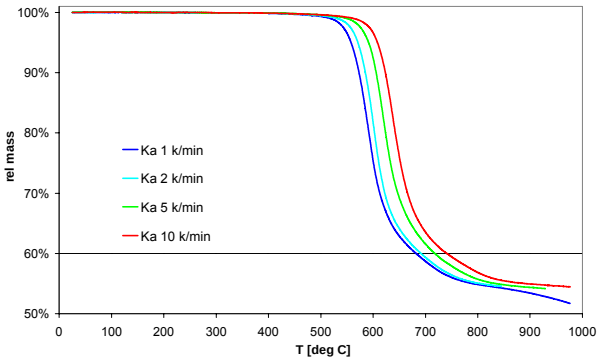

Fig. 1: TGA temperature scans of Kapton HN.

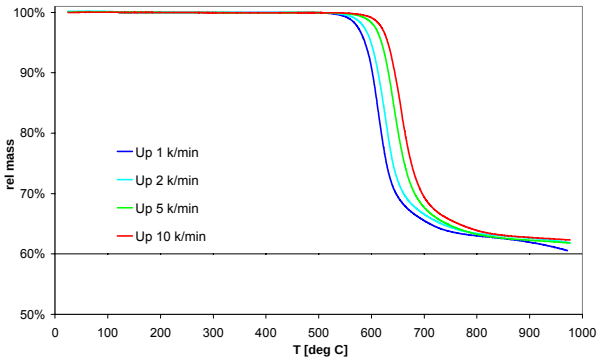

Fig. 2: TGA temperature scans of Upilex S.

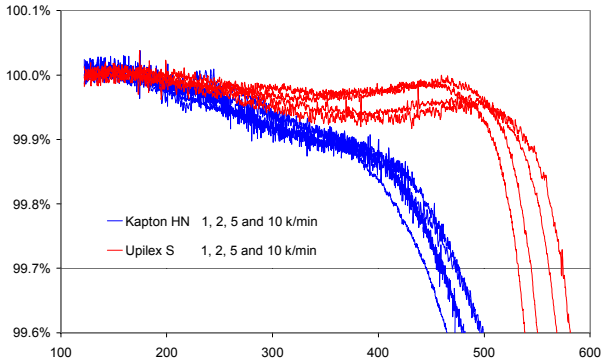

Fig. 3: Comparison of TGA temperature scans.

From these graphs a few conclusions can be drawn:

- The amount of residual mass, after the material is fully decomposed, is lower for Kapton HN (54.6 %) than for Upilex S (62.4 %).
- The decomposition starts at a lower temperature for Kapton HN (around 400 ºC) than for Upilex S (around 500 ºC).
- Before the actual decomposition takes place, mass loss is mostly due to outgassing/offgassing of molecules with a low molecular weight. This reaction becomes distinguishable between the two materials at a temperature of around 300 ºC, as shown in Fig. 3. At the temperature of interest, around 350 ºC, Upilex S shows less mass loss than Kapton HN.
- Two temperatures that are commonly used to assess and compare the thermal stability of materials are the temperature where 5 % of the total mass has decomposed (T_5) and the temperature where the rate of decomposition is the highest (T_{max}). These temperatures are higher for Upilex S than for Kapton HN, as indicated for the 10 °C/min heating rate in Table 1.

Table 1: Two characteristic temperatures to compare the thermal stability at 10°C/min.

Material	T_5 [°C]	T_{max} [°C]
Kapton HN	608	631
Upilex S	631	662

2.2. Isothermal tests

Two long duration isothermal test runs of both materials are shown in Fig. 4. The curves are normalised to discard the rather arbitrary effects of

desorption of humidity during conditioning steps and buoyancy during the heating of the furnace.

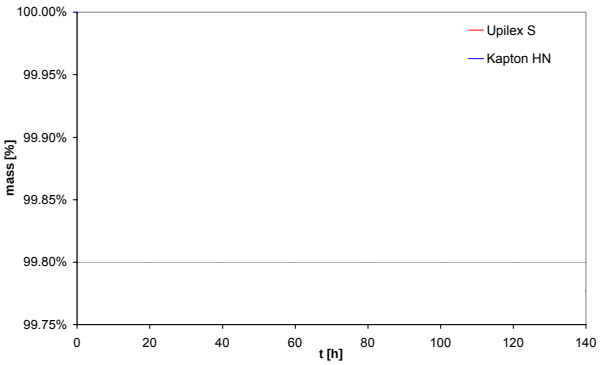

Fig. 4: Isothermal TGA runs at 350 °C.

It is clear that the mass loss of these samples at this temperature is on the limit of the 0,1 µg resolution of the balance of the TGA. Drifting of the balance signal is also a problem during long term testing. Nevertheless, the tendency of the curves is obvious. At a temperature of 350 °C, Upilex S looses less mass than Kapton HN.

It is difficult to extrapolate these curves to long durations (years) or to other temperatures and the experiments are very time consuming. The kinetic modelling of decomposition curves offers a quicker and more accurate result.

3. KINETIC MODELLING

The kinetic modelling is based on at least three decomposition curves at different heating rates. Usually, four TGA temperature scans are used at heating rates of 1, 2, 5 and 10 °C/min. In this paper two different approaches for the modelling are presented: the method described in ASTM E 1641 [2] and the method of Model Free Kinetics (MFK) [4, 5]. More details about the theoretical and mathematical background can be found in [4-9].

3.1. ASTM E 1641

The kinetic modelling of the decomposition reactions can be performed according to ASTM E 1641. The model is based on the Arrhenius equation in Eq. 1 and it is only valid for single decomposition reactions.

$$\frac{d\alpha}{dt} = A \cdot e^{\frac{-E}{RT}} \qquad (1)$$

where

α	:	conversion level	[%]
$d\alpha/dt$	:	reaction rate	[min^{-1}]
A	:	pre-exponential factor	[min^{-1}]
E	:	activation energy	[J mol^{-1}]
R	:	gas constant	[J mol^{-1} K^{-1}]
T	:	temperature	[K]

From the mass loss curves in Fig. 1 and 2, the conversion is calculated. This is the mass loss at a certain temperature relative to the mass loss that occurred after the sample has been fully decomposed. Thus, the conversion curves range from 0 % (no mass loss) to 100% (fully decomposed sample). The temperatures of constant conversion or isoconversion points are the temperatures at which a constant level of conversion is reached for all four heating rates. This is done for 1, 2.5, 5, 10 and 20% conversion in the so-called common thermogram that is shown for Kapton HN in Fig. 5.

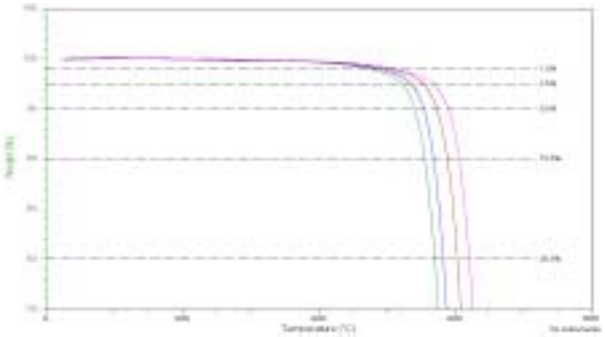

Fig. 5: Common thermogram of Kapton HN

The temperatures of constant conversion can be plotted as the logarithm of the heating rate versus the reciprocal absolute temperature. A linear curve fit of the four isoconversion points for all isoconversion levels (1, 2.5, 5, 10 and 20%) results in the Arrhenius presentation.

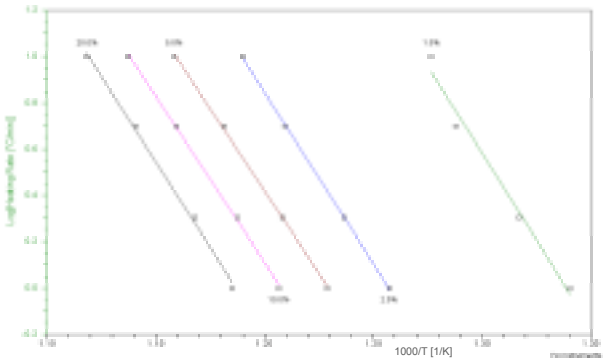

Fig. 6: Arrhenius presentation of Kapton HN

The Arrhenius presentation may be used to verify the kinetic modelling of the experimental results and to check the precision of the individual measurements. The data points should fit closely to the (fitted) straight line. If the data points are curved, failure to fit the model is indicated. If the data is scattered, additional experiments may be needed to improve the results. Furthermore, the slope of the respective lines should be parallel, if a single reaction mechanism fits all of the conversion levels.

The 1 % conversion data of Kapton HN in Fig. 6 shows the curvature as discussed above. This indicates that the data does not follow an Arrhenius law and its use for modelling is doubtful. The other datasets of isoconversion points seem to fit quite well.

The kinetic parameters E and A are derived [6] for all conversion levels from the slope of the corresponding curve in the Arrhenius presentation. They are shown for the 5% conversion level in table 2. This level of conversion is usually taken as a criterion to assess the lifetime of a material. At this conversion the activation energy of Upilex S is higher than of Kapton HN.

Table 2: Kinetic parameters calculated for the 5% conversion level.

Material	E [kJ/mol]	Log A
Kapton HN	250	13.5
Upilex S	312	16.8

The kinetic parameters are used to calculate [7] the lifetime predictions in Fig. 7 and 8. The lifetime curve is a linear fit if the conversion level is plotted on a logarithmic time axes versus the reciprocal absolute temperature. This plot indicates the time it takes to reach a certain level of conversion at a certain temperature.

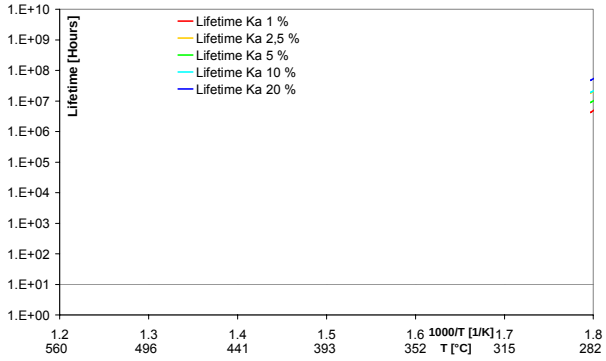

Fig. 7: Lifetime prediction Kapton HN

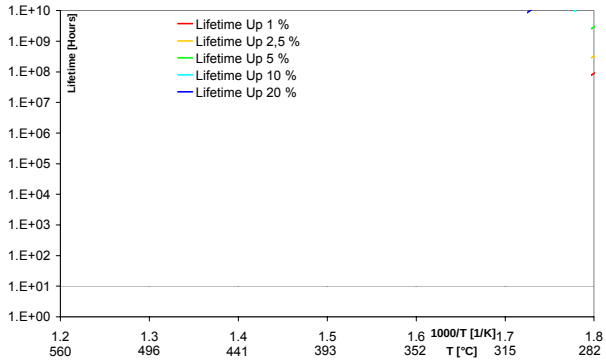

Fig. 8: Lifetime prediction Upilex S

In Fig. 7 it can be seen that the 1 and 2.5% conversion levels of Kapton HN are intersecting with the other curves. This can be a reason to discard the modelling results based on these datasets.

A direct comparison between the two materials is shown for the 5% conversion level in Fig. 9. This graph shows that at a temperature of 350 °C Upilex S reaches 5% conversion after a much longer duration than Kapton HN. The absolute values of these lifetime predictions should be used carefully. In this case, the largest source of errors is the fact that the 5% conversion data is retrieved from measurements done in the temperature range of 550 to 610 °C whereas the lifetime prediction is extrapolating the model to 350°C.

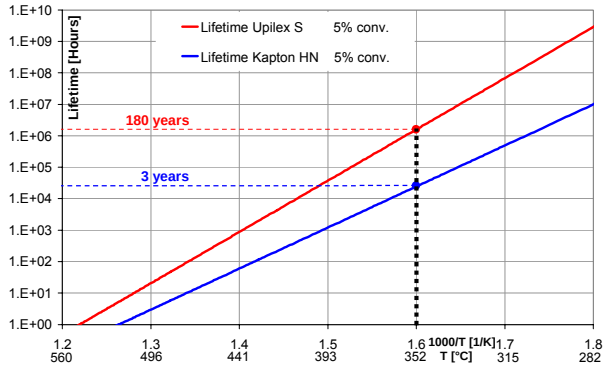

Fig. 9: Comparison of lifetime of both materials for 5% conversion level

One way of verifying the modelling is to calculate the "60 minutes half-life temperature" (T_{60}). This is the temperature at which 50% conversion occurs after an isotherm of 60 minutes. The calculated T_{60} is shown in Table 3. The isotherms at these temperatures are plotted for both materials in Fig. 10. The measured mass loss after 1 hour should correspond to the

predicted 50% conversion. The measured conversion in Table 3 compares quite well to the predicted 50%.

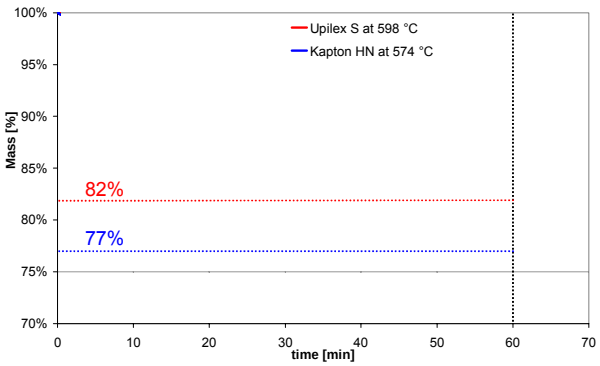

Fig. 10: 1 hour isotherms at T_{60} of both materials.

Table 3: Verification of conversion level after 1 hour isotherm at 60 minutes half-life temperature.

Material	T60	Residual Mass	Conversion
Kapton HN	574 °C	77 %	51 %
Upilex S	598 °C	82 %	48 %

3.2. Model Free Kinetics

The MFK approach is based on the temperature at a certain conversion [4]. Each conversion delivers a value for the activation energy. Therefore the activation energy is no longer a constant but it becomes a function of conversion. No assumptions are made with respect to the kinetic models. The Arrhenius equation for the temperature dependence of the reaction rate is still valid (see Eq. 1).

$$\frac{d\alpha}{dt} = A \cdot e^{\frac{-E(\alpha)}{RT}} \cdot f(\alpha) \qquad (2)$$

where $E(\alpha)$: activation energy [J mol^{-1}]
$f(\alpha)$: reaction model

In Fig. 11 the calculated [8] activation energy curves of both materials are compared. The part of the graph that is important in assessing the service temperature of these materials is at low conversions. It can be seen that until 20 % conversion the activation energy of Upilex S is higher than of Kapton HN. Below 5 % conversion the measured data becomes less accurate, which results in an activation energy that tends to go to zero. This cannot be correct since the reaction rate would then become independent of the temperature, see Eq. 2. Therefore a tangential correction is used to extrapolate the activation energy to low conversion.

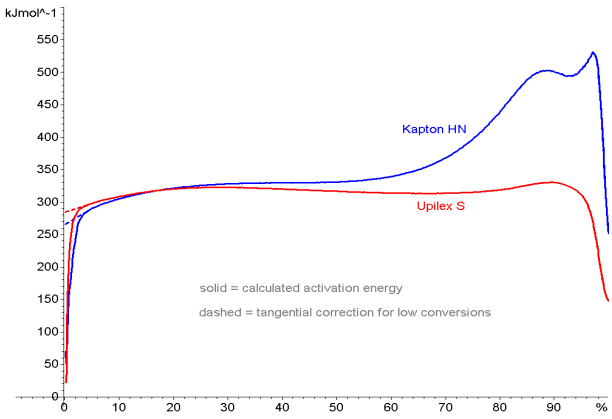

Fig. 11: Comparison of E(α) of both materials and extrapolation to low conversion.

The activation energy as a function of conversion and its tangential correction to low conversions are used to calculate [9] the lifetime predictions. A comparison of the predictions of 5 % conversion is shown in Fig. 12.

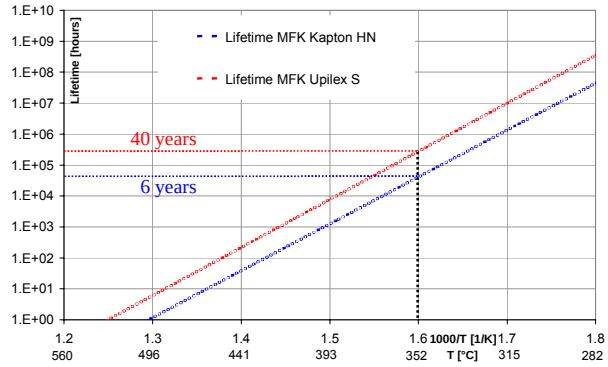

Fig. 12: Comparison of lifetime of both materials for 5% conversion level.

Upilex S reaches 5 % conversion at 350 °C after a duration that is approximately one order of magnitude bigger than in the case of Kapton HN.

3.3. Comparison of the two models

To compare the kinetic modelling by the ASTM E 1641 to the MFK, the activation energies are compared for the 5 % conversion level in Table 4. In Fig. 13 the lifetime predictions of both materials calculated by

both methods are overlaid. It should be noted that the experiments for the modelling were performed on different instruments. This comparison is done to get an idea of the error margins.

Table 4: Comparison of activation energy and lifetime predictions calculated by both models for 5 % conversion.

Material	Model	E [kJ/mol]	Lifetime [years]
Kapton HN	ASTM E 1641	250	3
	MFK	290	6
Upilex S	ASTM E 1641	312	180
	MFK	300	40

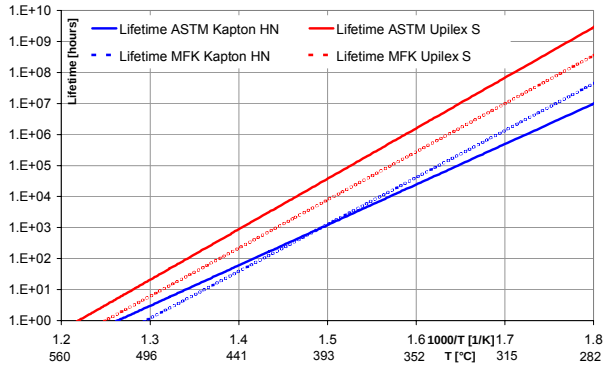

Fig. 13: Lifetime predictions of both kinetic models for both materials at 5 % conversion.

The kinetic modelling by MFK has some advantages compared to the ASTM E 1641 method:

- For most decomposition processes the activation energy is better described by a variable function of the conversion than by a constant value.
- The MFK is not assuming a first order reaction. Therefore it is possible to model more complex reactions.
- For low conversions it is better to base the lifetime prediction on the tangential extrapolation, which is possible for the MFK, than on data that is influenced by measurement inaccuracies.
- The MFK is using all of the measured TGA data to calculate the activation energy as a function of conversion, whereas the ASTM uses only a single data point and all other information is discarded.

4. COMPARISON OF MFK PREDICTIONS TO ENVIRONMENTAL TESTS

Samples of both materials were included in two environmental testing programmes [10]:

- HITES: High Temperature Exposure System
  Thermal ageing at 350 °C in a high vacuum chamber for durations up to 4452 hours.
- SUV: Solar UltraViolet facility
  Thermal ageing at 350 °C in a high vacuum chamber together with 3 solar constants of UV radiation for a duration of 675 hours.

In Tables 5 and 6, it is shown that the measured mass losses compare well to the predictions calculated by the MFK. However, no additional effects of the vacuum and the UV irradiation can be resolved on the mass measurements with the given error bars. It should be noted that different sample setups are used in the TGA, HITES and SUV.

Table 5: Mass losses in the HITES programme compared to the MFK predictions.

Material	Duration [h]	HITES		MFK
		Mass loss [%]	Conversion [%]	Conversion [%]
Kapton HN	2674	1.1 ± 0.4	2.5 ± 0.8	2.0%
Upilex S	4452	0.0 ± 0.3	0.0 ± 0.9	0.4%

Table 6: Mass losses in the SUV programme compared to the MFK predictions.

Material	Duration [h]	SUV		MFK
		Mass loss [%]	Conversion [%]	Conversion [%]
Kapton HN	675	0.44 ± 0.06	1.0 ± 0.1	1.2
Upilex S	675	0.08 ± 0.02	0.22 ± 0.06	0.27

5. CONCLUSIONS

Two polyimide materials that are planned to be used as thermal control foils on inner solar system planetary missions are tested for their thermal endurance. One is Kapton HN of DuPont and the other is Upilex S of UBE Industries. The decomposition reactions of the materials are measured as mass loss versus temperature curves with a nitrogen-purged TGA at heating

rates of 1, 2, 5 and 10 °C/min. The kinetics of the decomposition reactions is modelled by two methods: ASTM E 1641 and MFK. These models provide a lifetime prediction of the material that indicates the level of conversion at a certain temperature after a certain duration. According to the kinetic modelling Upilex S is about an order of magnitude better than Kapton HN: 5% conversion at 350 °C is predicted by the ASTM method after 3 years for Kapton HN and after 180 years for Upilex S and by the MFK method after 6 years for Kapton HN and after 40 years for Upilex S.

The predictions of the modelling are in good agreement with isothermal TGA tests at the 60 minutes half-life temperatures and with mass measurements in two environmental testing programmes. The MFK approach seems to be a more adequate method for kinetic modelling than the ASTM method. All experiments (TGA temperature scans, isothermal TGA tests, both kinetic modelling methods and the environmental exposures) in this comparative study show that Upilex S has a better thermal endurance than Kapton HN.

6. REFERENCES

[1] M. Moser, et al., *The use of kinetic modelling as a fast way to screen thermal endurance of space materials*, Proceedings of 9th ISMSE, The Netherlands, 2003

[2] ASTM E 1641-99, *American Society for Testing Materials*, USA 1999

[3] ASTM E 1877-00, *American Society for Testing Materials*, USA 2000

[4] S. Vyazovkin, *Thermochem. Acta*, (1992), 194

[5] M. S. Kelsey, *American Laboratory*, (1996), 13

[6] J. H. Flynn, L. H. Wall, *Polym. Lett.*, Vol. 4 (1966), 323

[7] J. H. Toop, *IEE Trans. Elec. Insul.*, Vol EI-6 (1971), 95

[8] S. Vyazovkin, *J. Comput. Chem.*, Vol 18, No. 3 (1997), 393

[9] S. Vyazovkin, *J. Comput. Chem.*, Vol 22, No. 2 (2001), 178

[10] C. O. A. Semprimoschnig, et al., *Space environmental testing of thermal control foils at extreme temperatures*, Proceedings of 9th ISMSE, The Netherlands, 2003