# A DETAILED STUDY IN THE THERMAL ENDURANCE OF POLYIMIDE RESIN MATERIALS

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## ABSTRACT

Among the industrial aeronautic polymers with high heat resistance, polyimide materials occupy a leading place up to temperatures of 300-400°C. Polyimides are commonly used in space application in the form of various molded articles, thin films and adhesive tapes. A particularly promising application is in bulk resin materials with their structural performance, shape retention and thermal stability in space ultra-lightweight system. In order to assess the thermal stability of polyimides, an experimental study was undertaken to investigate and predict the long-term behaviour of those materials by thermal analysis.

The polyimide materials have been provided by different suppliers and have been studied by thermogravimetry analysis (TGA) with dynamic temperature scans from room temperature to 900°C at different heating rates and with isothermal exposures with the view to determine the temperature limits of serviceability and establishing the prediction of thermal endurance on a time interval not easily accessible experimentally. The Advance Model Free Kinetics (AMFK) modelling has been used to model the lifetime prediction of the polyimide resins. The AMFK approach is based on the fact that the activation energy does not remain constant during a reaction but changes and that the activation energy at a particular conversion is independent of the temperature program (the “iso-conversion principle”). The results showed that for low mass loss value and up to 300°C no significant difference of the thermal endurance can be observed within the different polyimide resins but around 350°C the thermal endurance of the polyimide resins may vary by an order of magnitude. Moreover the process of baking at 300°C one of the tested polyimide resin for 48 hours limited the adsorption of the moisture and shifted the lifetime predictions curves resulting in improved thermal endurance of this resin even for low mass loss value.

## 1. INTRODUCTION

The purpose of this research is to assess and compare the thermal stability of the Meldin 7001 resin with UBE 201 and Vespel. The temperature range of interest is from room temperature up to 350°C. The mass loss of the material is measured over temperature scans with different heating rates and over 36 hours of isothermal exposure at 800°C by TGA. In addition the long term isothermal testing is compared with a kinetic modelling utilising the decomposition reactions from TGA temperature scans at several heating rates. With the AMFK model the lifetime prediction of the material can be made to predict the time it takes to reach a certain level of decomposition at a certain temperature.

## 2. TEST MATERIALS

### 2.1 Starting materials

Aromatic polyimides have been widely investigated for aerospace applications and microelectronics etc. due to their outstanding combinations of mechanical and thermal properties [1, 2]. During the past few years most of the investigations was focussed on thin polyimide films [3, 4, 5] resulting in high dimensional stability, low thermal expansion and wide range thermal stability. In this study bulk polyimide resins have been tested at high temperature.

Vespel was kindly supplied by DuPont, Meldin 7001 was kindly supplied by Carbone Lorraine., and 201 resin was kindly was kindly supplied by UBE Industries, Ltd. and used as received or after a cure at 300°C for 48 h in $N_2$.

### 2.2 Measurements

Specimens were analysed using thermogravimetric analysis (TGA). TGA was carried out with a Mettler-Toledo TGA/SDTA851$^e$ operating with the STAR$^e$

software using a heating programme from 25°C up to 900°C at four different ramp rates; 2°C.min$^{-1}$, 5°C.min$^{-1}$, 10°C.min$^{-1}$ and 20°C.min$^{-1}$. The furnace was continuously purged with nitrogen gas at a flow rate of 70ml.min$^{-1}$. Buoyancy and baseline corrections were made using a second run of the same sample (which should then no longer show any reaction) using the same method. All tests were performed in accordance with ISO specification 11358 [6].

## 3. EXPERIMENTAL RESULTS AND DISCUSSION

### 3.1 TGA results

Four different heating rates were selected to enable kinetic modelling and lifetime prediction for the materials analysed using Vyazovkin's Model Free Kinetics (MFK) approach [7]. All of the resultant thermograms were normalised with respect to sample mass and plotted against sample temperature. Up to 120°C the mass loss of the material is mostly due to evaporation of the moisture that was adsorbed on the surface of the material. This adsorption contributes to less than 0.3% of mass loss from 25°C up to 120°C, except for the 201 resin, with 1.1% of mass loss. To limit the water adsorption of the UBE 201, the resin has been baked in $N_2$ at 300°C for 48 hours before measurements. Above 450°C, TGA measurements have shown that polyimide materials such as 201, 201 cured, Vespel, Meldin 7001 display a single step decomposition process with a total mass loss value around 38% In Fig.1 a comparison of all the studied polyimide materials is plotted. This shows that the different polyimide materials can be separate into two groups depending of their temperature stability:

- Group 1: UBE 201 and UBE 201 baked
- Group 2: Vespel and Meldin 7001

The amount of mass loss, after the material is fully decomposed of the investigated materials is shown in Table 1. Those values are derived from temperature scans at 10 C/min.

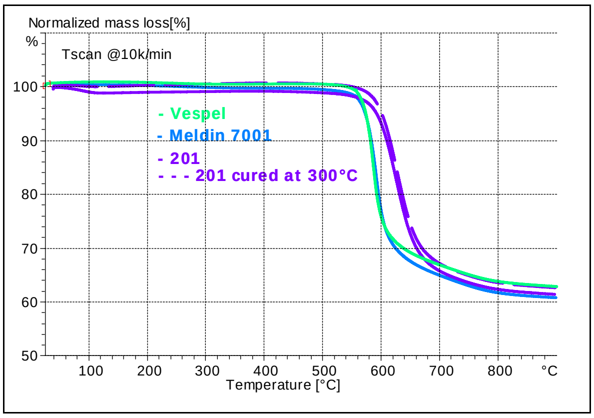


Fig.1 Comparison of normalized tscan curves at 10 °C/min of polyimide materials

Table 1: Comparative value of the main important values of polyimide materials

| Material | Absolute mass loss [%] | Range of the main decomposition temperature [°C] | Critical decomposition temperature [°C] |
|---|---|---|---|
| UBE 201 | 36.6% | 520-800°C | 625°C |
| UBE 201 baked | 36.6% | 530-800°C | 630°C |
| Vespel | 37% | 520-800°C | 590°C |
| Meldin 7001 | 38.7% | 520-800°C | 595°C |

### 3.1 Thermal endurance analysis

The lifetime predictions discussed within this paper have been derived from an MFK iso-conversional approach developed by Vyazovkin [8].Thermal decomposition of a solid material such as a polymer involves the chemical breakdown of the material, transportation and removal from the specimen. All of these processes will be kinetically driven and therefore have a minimum activation energy ($E_a$) required to allow the reaction to initiate. The MFK approach is based on conversion value at a certain temperature. Each conversion value delivers a specific activation energy value. Solid state kinetics can be generalised to an equation form which takes into account the dependence of the reaction rate on the extent of reaction (see Eq.1):

$$\frac{d\alpha}{dt} = A.e^{\left(\frac{-E(\alpha)}{RT}\right)} f(\alpha) \qquad (1)$$

where $A$ is a pre-exponential factor,
$R$ is the universal gas constant,
$T$ is the temperature
$t$ is time
$\alpha$ is the degree of conversion or extent of reaction and $f(\alpha)$ is the reaction model, a function describing the dependence of reaction rate on the extent of reaction.

The study of the lifetime prediction is based on the Advanced-MFK analysis with the use of t-scan and isothermal measurements. The AMFK utilises a differential approach for prediction of the activation energy function compared to an integral approach for the MFK analysis [4]. The AMFK technique requires the inclusion of at least one isothermal run and generally results in improving lifetime predictions particularly at low conversion values. An isothermal run was conducted at 600°C for 16 hours. Comparison of the lifetime prediction for Group 1 has been performed against Group 2 and shown in Fig.2**Error! Reference source not found.**. To enable comparison arbitrary mass loss values have been chosen (2.5%, 5% or 10% of mass loss) and converted into conversion values. For instance 100% conversion for 201 resin (as well as for 201 cured) gives 36.6% mass loss but for Vespel and Meldin 7001 37% and 38.7% respectively (See Table and Table 3)

Table 2 Comparison of equivalent mass loss values for 100% conversion

| Material | 100% Conversion value (%) |
|---|---|
| UBE 201 | 36.6 |
| UBE 201 baked | 36.6 |
| Vespel | 37 |
| Meldin 7001 | 38.7 |

Table 3: Equivalent mass loss conversion values

| Mass Loss (%) | Conversion Value (%) | | | |
|---|---|---|---|---|
| | 201 | 201 cured | Vespel | Meldin 7001 |
| 2.5 | 1% | 1% | 1% | 1% |
| 5 | 2% | 2% | 2.% | 2% |
| 10 | 4% | 4% | 4% | 4% |

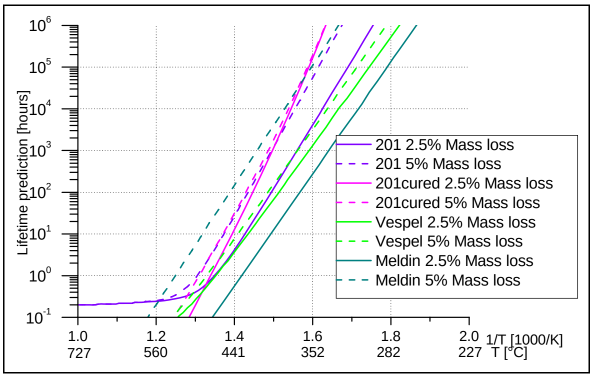

Fig 2. Comparison of lifetime prediction of the studied polyimide materials at 2.5% and 5% mass loss

Table 4 Comparison of the thermal endurance of all the studied polyimide materials (Approximate ±10%)

| **Mass loss [%]** | **Target exposure temperature [°C]** | **Endurance (hours)** | | | |
|---|---|---|---|---|---|
| | | **UBE 201** | **UBE 201 baked** | **Vespel** | **Meldin 7001** |
| 2.5 | 300 | $10^6$ (114 years) | $>10^6$ | $3x10^5$ (34 years) | $8x10^4$ (91 years) |
| | 350 | $5x10^3$ (210 days) | $2x10^5$ (23 years) | $10^3$ (42 days) | 200 (8 days) |
| 5 | 300 | $>10^6$ | $>10^6$ | $10^6$ | $>10^6$ |
| | 350 | $2x10^5$ (23 years) | $2x10^5$ (23 years) | $2x10^4$ (2 years) | $6x10^4$ (7 years) |

In fig.3, the two UBE 201 materials show a relatively good thermal endurance for high temperature especially with a lifetime prediction estimated round 2x $10^5$ hours (23 years) at 350°C for mass loss degradation value of 5%. A noticeable difference between the 201 cured and not cured resins can be pointed as for the 2.5% mass loss value at 350°C prediction values of $5x10^3$ hours (0.5 years) for the UBE 201 resin and of $1x10^5$hours (11.4 years) for the UBE 201 baked resins can be observed. The process of curing the 201 resin at 300°C for 48 hours limited the adsorption of the moisture (1% to 0.3 % of water mass loss) and shifted the lifetime predictions curves to the left resulting in improved thermal endurance of the 201 resin even for low mass loss value (2.5%)

The comparison of Vespel lifetime with the predictions for Meldin 7001 shows that for lower temperature range than the one targeted for this study (temperatures above 300°C) the thermal endurance at 2.5% mass loss value is relatively good for both of the bulk resins with a least $2x10^5$ hours of lifetime prediction (11.8 years) but pretty poor at 350°C with less than a year of lifetime prediction. Despite a better thermal endurance behaviour of Meldin 7001 with regards of the one of Vespel for mass loss value above 5% it is cleared that for low mass loss value such as 2.5% Meldin 7001 can not compete with Vespel. It would be perhaps interesting to cure the Meldin 7001 at 300°C to improve its thermal endurance and shift the 2.5% mass loss lifetime prediction to the left.

## 4. CONCLUSION

Polyimide resin issued from UBE industries showed significant endurance lifetimes at 350°C (> 100 years). The process of curing the UBE 201 resin at 300°C for 48 hours limited the adsorption of the moisture (1% to 0.3 % of water mass loss) and shifted the lifetime predictions curves to the left resulting in improved thermal endurance of the 201 resin even for low mass loss value (2.5%).Vespel and Meldin 7001 have relatively good and comparable thermal endurance From this study it is apparent that UBE 201 baked and UBE 201 have significantly better thermal endurance than the others polyimide resins. The Vespel have the third position and the materials relative thermal endurance can be ranked as: UBE 201 baked > UBE 201> Vespel > Meldin 7001. Previous work performed at ESA/ESTEC showed that thermal endurance of some polyimide can be significantly improved by isothermal ageing. This was not done in this investigation and therefore these results constitute a worst case but could be improved by a baking process.

## 5. REFERENCES


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